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Baseline groundwater chemistry: the Chalk aquifer of Hampshire

Groundwater Resources Programme
Open Report OR/09/052

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GROUNDWATER RESOURCES PROGRAMME

OPEN REPORT OR/09/052

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Keywords

Baseline; Chalk; Hampshire; water quality; hydrochemistry; UK; aquifer.

Front cover

On-site measurements at Otterbourne Pumping Station [447520, 123220]

Bibliographical reference

STUART M.E. AND SMEDLEY P.L.. 2009. Baseline groundwater chemistry: the Chalk aquifer of Hampshire. *British Geological Survey Open Report*, OR/09/052. 61 pp.

Keyworth, Nottingham British Geological Survey 2009

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Foreword

Although groundwater has long been seen as a relatively pure natural resource stored in subsurface aquifers, its quality is under an ever-increasing threat from human influences. Changes in chemical quality occur through direct inputs of anthropogenic substances, through groundwater abstraction and resultant change in groundwater flow regimes and through artificial recharge. Groundwater is an important resource for drinking, agricultural, industrial and domestic supply. About 35 per cent of public water supply in England and Wales and more than 70% in south and east England is provided by groundwater resources. Groundwater flows and seepages are also vital for maintaining summer flows in rivers, streams and wetland habitats, some of which rely solely on groundwater. Monitoring, management and protection of groundwater quantity and quality are therefore important economic and environmental priorities.

Characterisation and monitoring of groundwater chemistry is a critical component of management and protection. This provides the basis for defining the suitability of groundwater for its intended purpose, identifying pollution inputs and assessing any temporal change. The main European driver for the characterisation and monitoring of groundwater quality is European Union legislation in the form of the Water Framework Directive, Groundwater Directive, EC drinking-water regulations and environmental-quality standards. A key starting point for aquifer protection is defining the natural or 'baseline' chemistry of the groundwater body concerned. This sets the framework against which anthropogenic impacts and trends can be measured.

The concept of 'baseline' in the context of groundwater quality is difficult to define in detail and opinions differ on the meaning and application of the term. The presence of purely anthropogenic substances such as pesticides or CFCs indicates a departure from the natural condition, but for many solutes which can be derived either from pollution or natural sources, for example nitrate, phosphorus or arsenic, the distinction is less clear-cut. In addition, specific chemical constituents in a given groundwater body may be identified as pollutants while other component solutes may be entirely naturally-derived. For the purposes of this study, baseline is defined as:

> "*the range in concentration (within a specified system) of an element, species or chemical substance present in solution which is derived by natural processes from natural geological, biological, or atmospheric sources*".

The baseline chemistry of groundwater varies widely as a function of the many complex geological, geochemical, hydrogeological and climatic factors. These give rise to large spatial and temporal variations in chemical quality, at a range of scales. Hence, the baseline for a given element or compound will vary significantly both between and within aquifers. It is, therefore, scale-dependent and should be considered as a range rather than a single value.

Attempting to define the natural baseline chemistry of groundwater from a number of defined aquifers or aquifer regions in England and Wales has been the objective of the 'Baseline' project. The project involves the characterisation of spatial and temporal variations in groundwater chemistry and interpretation of the dominant controlling processes within a given area, aquifer or aquifer block. For each study area, this has been achieved through collation of existing reliable groundwater, rainfall, land-use and host-aquifer mineralogical and geochemical data, as well as new strategic sampling of around 25–30 groundwater sources for a comprehensive suite of inorganic constituents. Selected analysis of stable isotopic compositions (e.g. O, H, C) and atmospheric tracers (CFCs, SF_6) has also been undertaken where appropriate. Statistical methods, including statistical summaries (medians, means, percentiles), together with box plots and cumulative-probability diagrams, provide some of the most valuable analytical tools for the assessment of chemical data and have been

used in the Baseline report series. The Baseline reports provide a summary of the inorganic chemical status of groundwaters in a given study area and key pressures on water quality which should provide useful background information of value to water regulators and managers, environmental scientists and water users.

The current series of Baseline reports has been produced by the British Geological Survey with funding from the Natural Environment Research Council. This follows on from a previous series which was produced in collaboration with, and with co-funding from, the Environment Agency.

Previous published reports in the Baseline Series (British Geological Survey – Environment Agency):

1. The Triassic Sandstone of the Vale of York
2. The Permo-Triassic Sandstones of West Cheshire and the Wirral
3. The Permo-Triassic Sandstones of South Staffordshire and North Worcestershire
4. The Chalk of Dorset
5. The Chalk of the North Downs
6. The Chalk of the Colne and Lee River Catchments
7. The Great and Inferior Oolite of the Cotswolds District
8. The Permo-Triassic Sandstones of Manchester and East Cheshire
9. The Lower Greensand of southern England
10. The Chalk of Yorkshire and North Humberside
11. The Bridport Sands of Dorset and Somerset
12. The Devonian aquifer of South Wales and Herefordshire
13. The Great Ouse Chalk aquifer
14. The Corallian of Oxfordshire and Wiltshire
15. The Palaeogene of the Wessex Basin
16. The Granites of South-West England
17. The Ordovician and Silurian meta-sedimentary aquifers of central and south-west Wales
18. The Millstone Grit of Northern England
19. The Permo-Triassic Sandstones of Liverpool and Rufford
20. The Permo-Triassic Sandstone Aquifer of Shropshire
21. The Chalk and Crag of North Norfolk and the Waveney Catchment
22. The Carboniferous Limestone of Northern England
23. The Lincolnshire Limestone

Reports in the current series

Baseline groundwater chemistry: the Carboniferous Limestone aquifer of the Derbyshire Dome

Acknowledgements

We would like to thank Peter Williams for assisting with the groundwater sampling. All chemical analysis was carried out at the BGS laboratory. Debbie Allen, Sally Bourliakas, Jenny Cook, Dan Lapworth and Peter Williams are thanked for major and trace element analysis. Thanks are also extended to Chris Milne for overseeing the analytical quality control, George Darling for conducting the analyses of stable isotopes (O, H, and C) and Daren Gooddy for analysis of atmospheric tracers (CFC, SF_6). We would also like to acknowledge the support from landowners as well as from staff members of the water industry, Southern Water, Southeast Water and Portsmouth Water, who provided us with data, access to their Hampshire boreholes and assistance with sampling.

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Summary

This study characterises the spatial and temporal variations in inorganic chemistry in the Chalk aquifer of Hampshire, spanning the area from Basingstoke in the north-east to Cadnam in the south-west. The investigation aims to assess the likely natural baseline chemistry of the groundwater by identifying the dominant controlling processes (natural and anthropogenic) including from biogeochemical reactions and pollutant inputs. Results have been collected from strategic sampling of 30 groundwater sources, in conjunction with collation of existing groundwater, rainfall, mineralogical and geochemical data.

The Hampshire Chalk forms a predominantly anticlinal structure which dips southwards beneath Palaeogene cover into the Hampshire Basin and northwards into the London Basin. It forms a regionally significant aquifer for potable and agricultural use and also provides baseflow to the Rivers Test and Itchen, which are used extensively for fishing.

The results show that groundwater is typical of unconfined Chalk groundwater, of Ca-HCO_3 type. Variations in the natural chemistry take place with increasing residence time as water moves away from the groundwater divide downgradient beneath the Palaeogene cover. There is a notable effect on groundwater chemistry from the Palaeogene cover in the south of the study area with slightly increased concentrations of Mg, K, SO_4, Br, F, Ba, Sr, Li, Rb, Se, Cr, Mo, Ni, U compared to outcrop Chalk groundwater.

Human impact is most plainly visible in the distributions of nitrate in the groundwater. These are regionally high, with one analysed source having groundwater above the EC/national drinking-water limit of 11.3 mg L^{-1} as N and time-series data demonstrating an increase in concentrations in some groundwaters over the last few decades. The widespread presence of nitrate indicates the extent to which the aquifer has been and continues to be influenced by farming practices. Other nitrogen species (NO_2 and NH_4) and P are present at slightly above concentrations that would be considered baseline in groundwater from the south-east of the study area, particularly the Meon valley. Concentrations of Cu and Zn are also present at relatively high concentrations (up to 31 µg L^{-1} and 253 µg L^{-1} respectively) in some groundwaters. This may be due to contamination from wellhead pipework rather than processes leading to accumulation within the aquifer.

1 Introduction

The Hampshire Chalk is a folded anticlinal structure that forms part of the Wessex Basin. The outcrop forms a landscape of small hills and shallow valleys. The Chalk is confined to both the north and south by overlying Palaeogene sediments.

The Test and Itchen valleys stretch north-south from the Chalk Downlands on the Berkshire border to the meadows and valleys of the rivers that discharge into Southampton Water and the Solent. The River Meon drains the area to the south-east and the River Loddon northwards from the Berkshire Downs into the London Basin. These catchments are predominantly rural areas with significant agricultural activity, but they also have an economy based on industrial and commercial communities, primarily in and around the main towns.

The Chalk forms a major aquifer, widely used for public supply. Only about 3% of abstraction is for industrial and agricultural production, including water-cress. The underlying Upper Greensand is also exploited in places. The majority of Chalk public supply boreholes are sited along the river valleys to exploit the shallow depth to the water table and the typically higher transmissivity in the river valleys.

Groundwater in the Test and Itchen catchments is assessed as being of poor chemical status under the Water Framework Directive due to rising concentrations of nitrate. There are also issues with availability of groundwater for abstraction, particularly towards the south-east of the area.

2 Geographical setting

2.1 STUDY LOCATION

The study area is situated in the central and northern parts of Hampshire covering the area from Basingstoke to south of Winchester and from Andover to the Meon Valley (Figure 2.1). The ground rises to around 200 to 250 metres above Ordnance Datum (m aOD) on the Berkshire/Wiltshire Downs along the north-west of the area, with a maximum at Haydown Hill (254m aOD). To the south-east the highest point occurs at Butser Hill (271 m aOD; Figure 2.1).

The central part of the area is mainly rolling countryside drained by the Rivers Test and Itchen, which reach the coast at Southampton. The River Meon drains the south-eastern part of the study area and the River Loddon the north-eastern part.

2.2 LAND USE

Agriculture has always played a large part in shaping the local landscape, which would originally have been forested. In the thirteenth century land was parcelled up into smaller fields, enclosed by banks, hedges and ditches, many of which are still visible today. Medieval land use still survives in places in the Test valley where old water meadows are now common land.

Large parts of the Chalk outcrop were enclosed during the 19th century to form medium to large straight-sided fields (data from Fairclough et al., 2002). The outcrop area remains primarily agricultural with a mixture of improved grassland for grazing for cattle and sheep, together with cereals and other field crops (Figure 2.2). The principal cereal crops are winter barley and wheat, with other crops being mainly oilseed rape, field beans and peas and some linseed (HCC and HEP, 2007). Production of pigs and poultry is also important. Horticulture accounts for less than 1% of the Hampshire land use and comprises vegetables and fruit. Historically there have been extensive watercress beds in the upper parts of the catchments of the Test and Itchen. These accounted for 70% of UK production. Recently, small vineyards have also developed (HCC, 2004).

The majority of wooded areas are on the Palaeogene outcrop in the south-west and north-east of the study area, but there are also wooded areas along the river valleys and scattered woodland elsewhere (Figures 2.3 and 2.4). A distinctive pattern of small, irregular fields within the surviving woodland is typical.

The valley of the Test has supported a variety of industries in the past, such as tanning and flour milling but the majority of these have declined. The rivers are now used extensively for trout and salmon fishing.

The last 125 years have had a major impact on the landscape of Hampshire (Fairclough et al., 2002). Large-scale urbanisation took place, expanding from long-standing centres of defence and trade at Portsmouth and Southampton. The growth of London and of surrounding military establishments has had an effect on the proliferation of urban and suburban growth in the northeast of the area. The study area extends to the northern edge of the major urban development of Southampton, with Eastleigh and Winchester extending northwards along the line of the present M3 motorway. The area also includes the Romsey, Basingstoke and Andover urban centres. Industries on the outskirts of Winchester developed in Victorian times with the building of the railway. Basingstoke and Andover significantly increased in size by development as new towns in the 1960s.

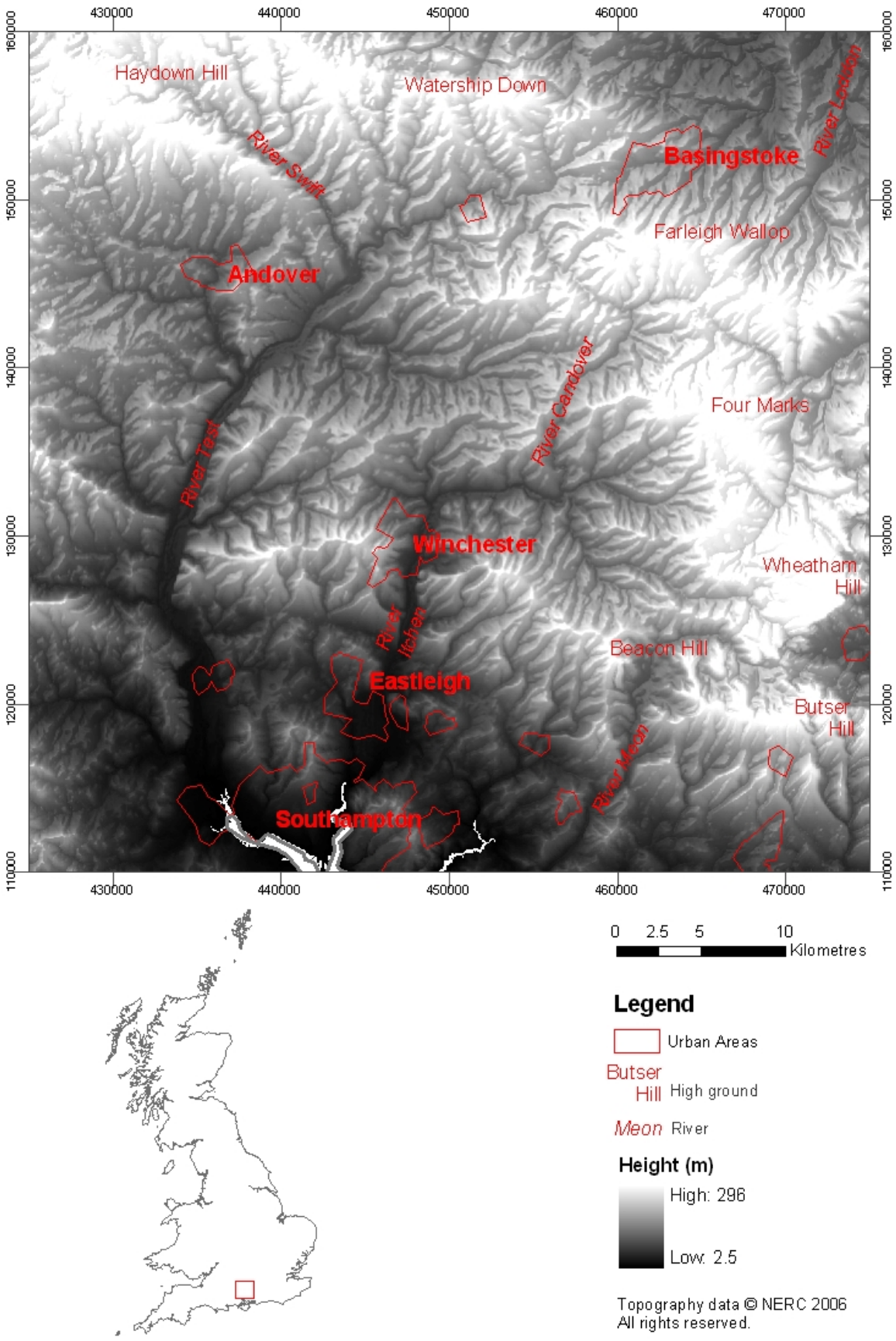

Figure 2.1 Location and topography of the study area

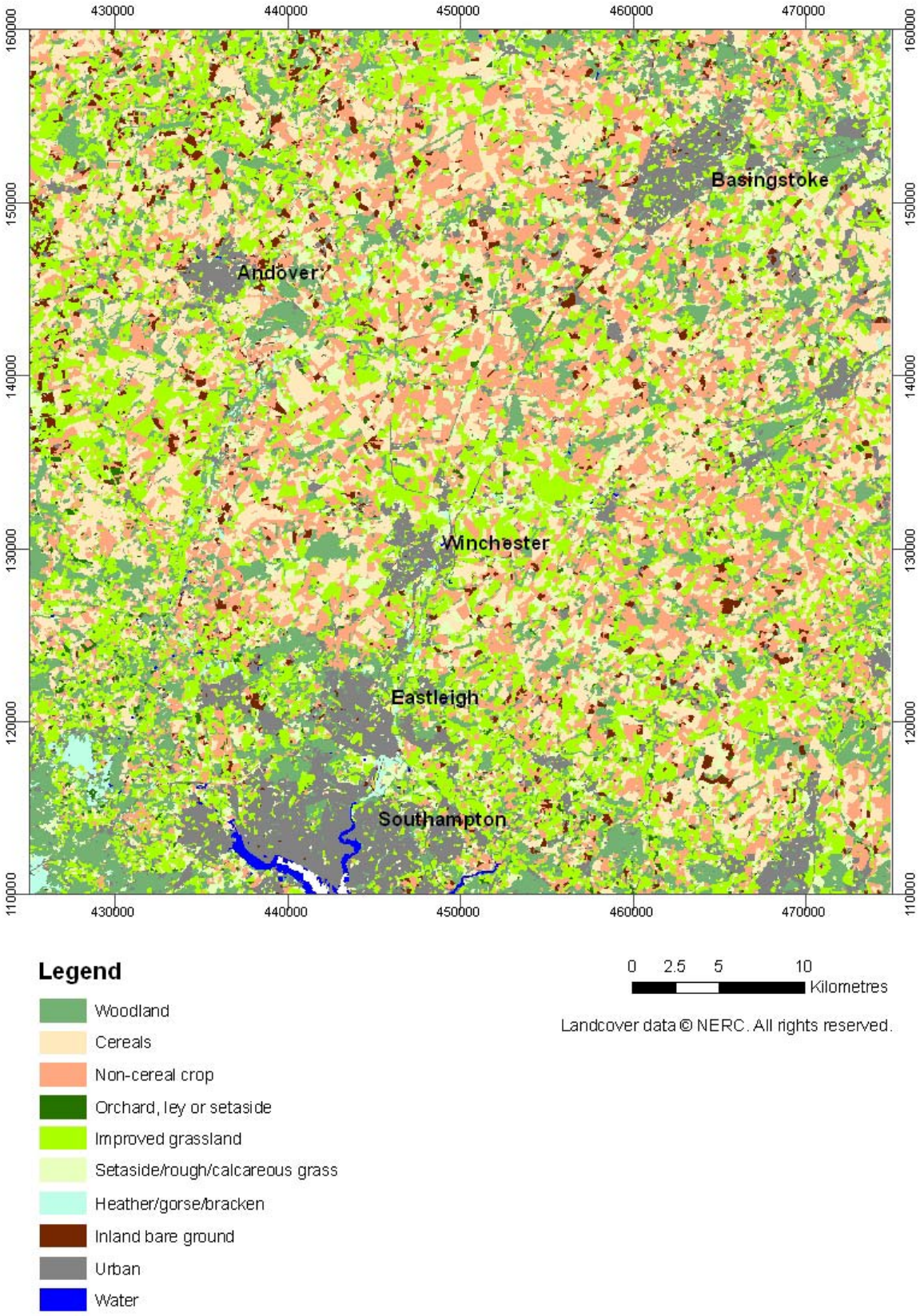

Figure 2.2 Land use in the study area (data from CEH, 2000)

Figure 2.3 View eastwards along the River Itchen from the bridge at Avington [SU 546 328]

Figure 2.4 View south-westwards from near Brook [SU 341 286] with the valley of the River Test in the middle distance

3 Background to the understanding of baseline chemistry

3.1 REGIONAL GEOLOGY

The Chalk outcrops in a broad north-west to south-east-trending band, with newer Palaeogene deposits to the south-west and north-east and older Greensand deposits to the east (Figure 3.1). Over much of this area, the outcrop consists of upper strata of the White Chalk Subgroup (the Newhaven, Seaford and Lewes Nodular Chalk Formations; broadly the former 'Upper Chalk'). These generally consist of white chalk with numerous flint seams. The underlying 'Middle Chalk' consists of white chalk with many marl beds (the New Pit Formation) underlain by hard, nodular, shelly chalk (the Holywell Nodular Chalk Formation). The Grey Chalk Subgroup (Lower Chalk) is predominantly marly. The map shown in Figure 3.1 is derived from digital cover at the 1:250,000 scale which currently employs the former Chalk classification and this is employed in this report where appropriate.

The exposed Chalk uplands are predominantly anticlinal in structure (Allen et al., 2009). There are several major west-east-trending fold structures that formed in response to compression during the Miocene inversion of the Wessex Basin. From south to north these comprise the Portsdown, Winchester–East Meon, Stockbridge and Kingsclere Anticlines, with the intervening Winchester–Kings Sombourne and Micheldever Synclines. These anticlines tend to be asymmetrical structures with strata dipping gently on the southern limb and more steeply on the northern limb. In places these anticlines are deeply eroded, providing elongated windows through the Middle Chalk into the Lower Chalk or the underlying Upper Greensand, for example at Cheesefoot Head near Winchester and at Kingsclere. The detailed morphology owes much to the existence of numerous subsidiary fault axes.

The Chalk dips southwards beneath Palaeogene cover into the Hampshire Basin and northwards into the Thames Basin. The Palaeogene Lambeth Group rests unconformably on the Chalk and consists mainly of mottled clay in the east of the area, becoming more sandy westwards. The overlying London Clay Formation comprises silty and sandy clay with interbedded cement stone and pebble beds and lenticular bodies of fine-grained sand. The Bracklesham and Barton Groups consist of interlayered sands and clays.

The Chalk in the northern and eastern parts of the catchments is covered by extensive amounts of Clay-with-flints, particularly the area to the east and north-east of Alresford (Figure 3.2). These deposits are present as coverings to interfluves in the west of the study area. Palaeogene gravels, sands and clays occur in southern areas and in places flinty solifluction deposits (head) occupy the valley bottoms. The valleys of the main rivers are filled with alluvium with some occurrences of calcareous tufa.

The map shown in Figure 3.2 is derived from digital cover at the 1:50,000 scale and therefore covers a number of geological sheets produced at different times. In the north and south-west of the area the head is not treated in the same way as the rest of the area.

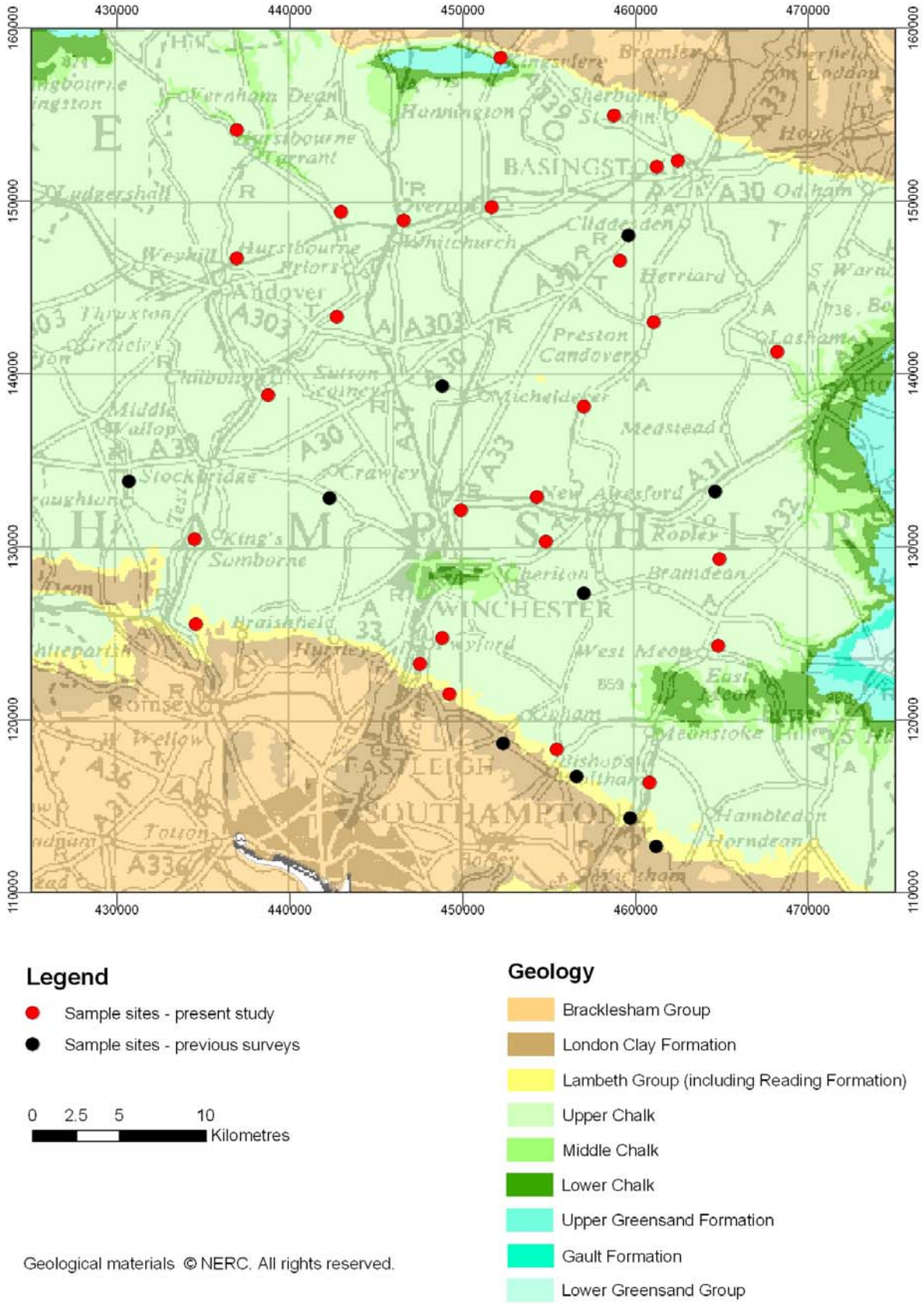

Figure 3.1 Solid geology of the study area and locations of sample sites

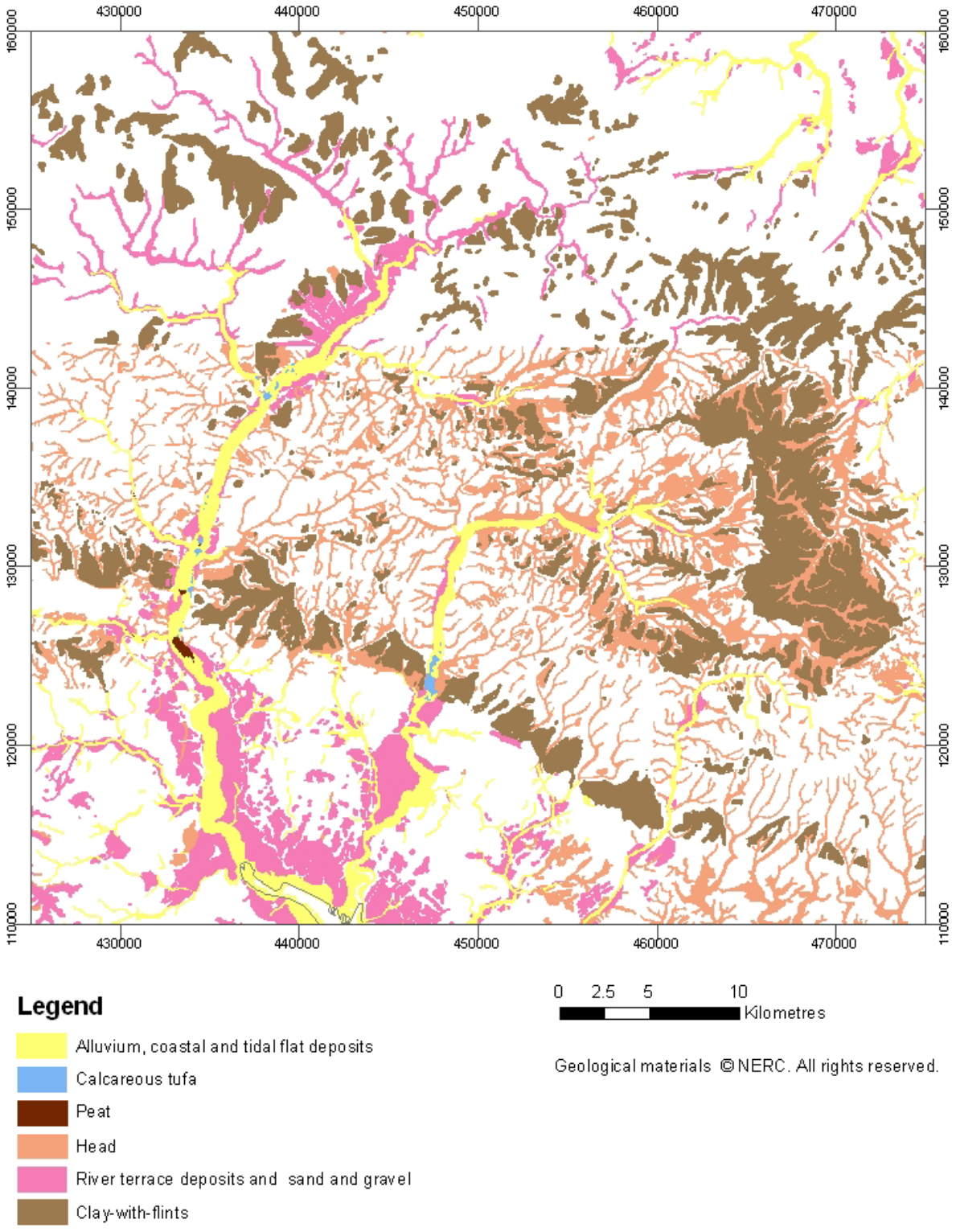

Figure 3.2 Superficial geology of the study area

3.2 REGIONAL HYDROGEOLOGY

The Chalk forms the major aquifer in southern England. The water table in the Hampshire Chalk generally follows a subdued form of the topography, with the unsaturated zone being thicker under hills and thinner in the valley areas (Allen et al., 2009). Groundwater contours shown on the hydrogeological map (IGS, 1979) generally indicate the expected flow of groundwater southwards to the main Test and Itchen river systems on their middle reaches prior to flowing over the Palaeogene deposits (Figure 3.3). Groundwater contours in the north indicate that discharge is northwards into the River Loddon. In the south-east, the Chalk drains to the River Meon. Where the Chalk is confined by Palaeogene strata the Chalk piezometric surface is not shown, but limited data from boreholes indicate a gradient to the coast.

Flow through the Chalk unsaturated zone takes place either by fracture flow or matrix flow or a combination of the two. Recharge to the aquifer through the unsaturated zone may also comprise both vertical and horizontal flow components. The dominating process of recharge is likely to be influenced by the presence of permeable or impermeable horizons within the Chalk. The overlying Palaeogene and Quaternary deposits also have an influence on recharge, with impermeable units likely to cause run-off, and the more permeable units allowing direct recharge to occur. The presence of impermeable deposits may also concentrate flow in certain areas and hence increase the amount of recharge to the underlying aquifer.

The analysis of soil physics data from a study at Bridget's Farm near Winchester concluded that water moves predominantly through the fine pores of the Chalk matrix with only a minor component through the fissures (Wellings, 1984a,b). Darling and Bath (1988) determined from δ^2H and $\delta^{18}O$ compositions in the unsaturated Chalk groundwater at Bridget's Farm that the matrix conductivity was high at this site.

Atkinson and Smith (1974) used groundwater tracing techniques to identify significant hydraulic connections between swallow holes and springs in the south Hampshire Chalk. This connectivity was considered to be the result of dissolution caused by rapid run-off from the Palaeogene cover, thereby enhancing the transmissivity of the Chalk. Lithology is an important control and the hydraulic properties are influenced by the presence of hardgrounds, flints and marl bands. Fissure zones appear to be associated with tabular flint bands in the Upper Chalk (Entec, 2002). Karst features have been observed in the Twyford cutting for the M3 motorway (Hopson, 2000). A palaeo-cave system partially filled with sediment was identified in the centre of the cutting and calcreted karst at the southern end along the main fractures and along the surfaces of hardgrounds and marls.

The Upper Chalk is generally considered a better aquifer than the Middle and Lower Chalks, although solution can increase the hydraulic properties of the Middle Chalk where it is near the surface. The Lower Chalk is a poorer aquifer due to a high marl content and limited fracture development. Where groundwater flow is predominantly through the Lower Chalk, as in east Hampshire towards the Weald, transmissivity is thought to be usually less than 500 m^2 day^{-1}. There is evidence that the Chalk and Upper Greensand are not in hydraulic continuity (Giles and Lowings, 1990).

Topography is also an important factor: yields from the boreholes sited in the interfluve areas are generally less than in the valleys. Transmissivity values of 1000 m^2 day^{-1} are common in the Upper Chalk in valleys but, together with storage coefficients, are thought to decrease away from the valley into the interfluves (Allen et al., 2009; Allen et al., 1997).

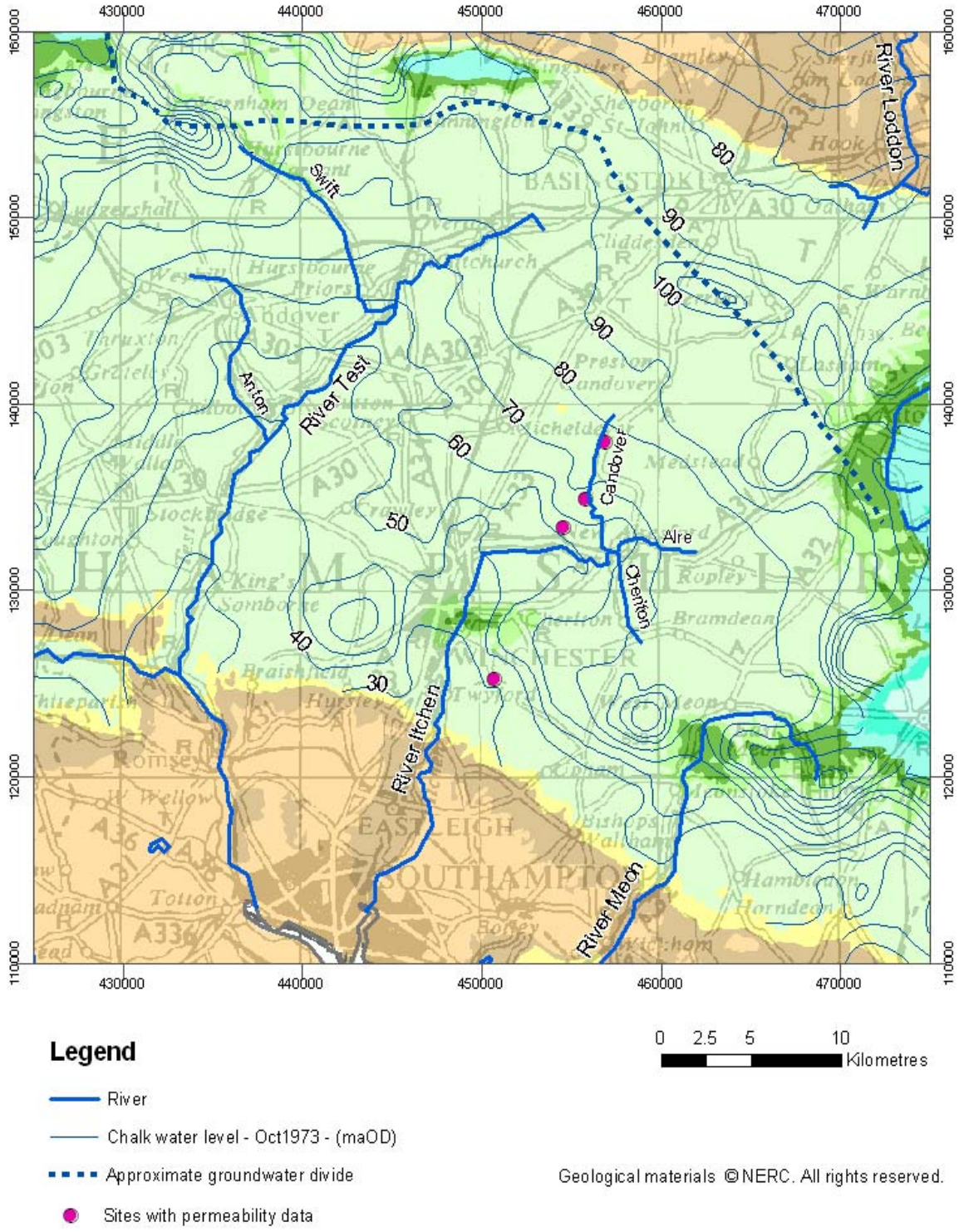

Figure 3.3 Surface drainage and groundwater contours for outcrop Chalk. Groundwater contours from IGS (1979).

Geological structure plays both a direct and indirect role in the development of aquifer properties. Some valleys develop along the axes of synclines or faults (SWA, 1979). Giles and Lowings (1990) suggested that higher yields develop along the axes of denuded synclines rather than anticlines.

Chalk porosity varies between about 5% and 45% and depends on stratigraphy (Bloomfield et al., 1995). For example, the Upper Chalk of southern England has an average porosity of

39%, the Middle Chalk 28% and the Lower Chalk 23 % (Bloomfield et al., 1995). In the Upper Chalk at Twyford, porosity of the Seaford Chalk is in the range 38–50% and that of the underlying Lewes Nodular Chalk between 35 and 40% (Stuart et al., 2008a).

Several studies have investigated the variability of aquifer properties with depth in this area. At Alresford in the Candover catchment, a study of artesian boreholes at watercress farms found that a narrow zone at the top of the boreholes was contributing the majority of the flow, with the rest of the aquifer providing upwards leakage to this high-transmissivity layer (Headworth, 1978). A detailed investigation of the River Itchen augmentation scheme showed a decrease in storage with water level. During the prolonged drought of 1976, an analysis of drawdowns from a group pumping test indicated that the aquifer was multi-layered. The 6-m thick top layer, just below the water table, had high transmissivity and storage. Beneath this was a layer with lower transmissivity and storage which constituted the remainder of the Upper Chalk.

Price et al. (1977) carried out detailed tests in three different boreholes in dry valleys in the Candover catchment, including core permeability testing, geophysical logging and packer injection testing (Figure 3.4a). The study for one of the boreholes showed that:

- the permeabilities measured from packer testing were one or two orders of magnitude greater than the core permeability;
- zones that had very high permeability corresponded to fracture locations;
- most of the saturated thickness of the Chalk had very low permeability: only a few fractures were required to give the total transmissivity;
- the most important flow horizons were near the top of the borehole with very little flow below 40 or 50 m bgl;
- there appeared to be little correlation between the high-transmissivity layers and Upper Chalk stratigraphy.

The observations contrasted with those for the aquifer in the adjacent Alre catchment which was not layered in the same way but had large-diameter fractures at various levels in both the Upper and Middle Chalk.

Packer testing of a borehole at Twyford found that the most important flow horizons occurred in the zone extending to about 10 m below the water table, with low values below this (Stuart et al., 2008a). Permeabilities were similar to those found in the Candover boreholes but with less variability. As with the Candover boreholes, the permeabilities estimated from packer testing were two or more orders of magnitude greater than the core permeability (Figure 3.4b).

The nature and extent of Palaeogene deposits will also influence the development of aquifer physical properties. For example, fracture apertures in the Chalk will be small under significant Palaeogene overburden resulting in lowered transmissivities.

Across the groundwater divide towards the Weald in east Hampshire, the transmissivity values are lower (usually less than 500 m^2 day^{-1}). This reflects the stratigraphy of the Chalk. Groundwater flow is predominantly through the Lower Chalk, which is less fractured. Storage potential is also reduced. The transmissivity improves on the scarp slope towards the Thames Basin in the north (Allen et al., 2009)

From a gas tracer study at Bridget's Farm (Darling et al., 2005) results of SF_6 and CFC analysis suggested that surface breakthrough occurred in less than 1 year after injection at 25 m depth. This implies a very open system where the groundwater age clock appears to start

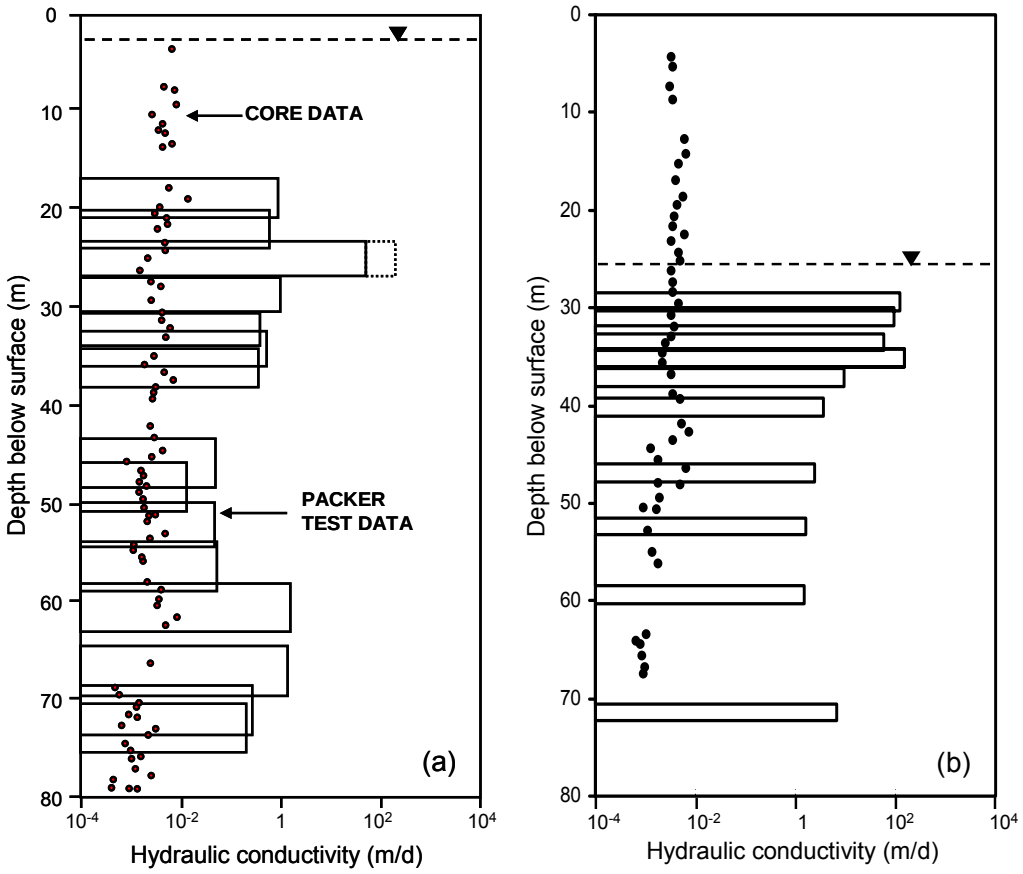

Figure 3.4 Vertical permeability profiles in core material compared with packer-test data; a) boreholes from Candover (Price et al., 1977); b) a borehole from Twyford (Stuart et al., 2008a)

as the water table is reached. Bulk groundwater recharge dates for samples from the Meon catchment area varied, from about 1966 at Lower Upham PS on the edge of the Palaeogene outcrop to 1985 at West Meon PS.

3.3 AQUIFER MINERALOGY

The Chalk is a microporous limestone comprising mainly coccolithic fragments with lesser amounts of other fossils and shelly debris. The coccoliths are composed of a relatively pure calcite. However, small amounts of other elements (Mg, Sr, and Mn) are present in the calcite structure. The chalk is composed of low-magnesium carbonate with an MgO content typically less than 0.4%. Original biogenic silica has undergone extensive diagenetic changes to form the typical flint bands of the Chalk.

The non-carbonate fraction of the Chalk comprises mostly clays, but minor amounts of zeolite, quartz, collophane, dolomite, feldspar and barite have been noted (Hancock, 1993). Significant amounts of clay and terrigenous material, dominantly smectite and quartz, are present in the Lower Chalk, (Bath and Edmunds, 1981). Of the clay minerals present, smectite dominates in most formations but is particularly abundant in the Upper and Middle Chalk (Morgan-Jones, 1977) where it often forms distinct marl bands containing as much as 30% clay (Hancock, 1993). Kaolinite is less abundant and is often considered to be detrital in origin (Morgan-Jones, 1977) although it may be derived in part from alteration of glauconite. Muscovite and illite are also considered to be detrital. Clays and iron oxides are extensively developed on shallow fracture surfaces (Shand and Bloomfield, 1995).

Table 3.1 Rainfall chemistry measured at Compton, Berkshire and Porton, Wiltshire (average of measured values 2000 to 2008; (NETCEN, 2008) and (ECN, 2008)). Concentrated rainfall (3× concentration factor) represents rainfall affected by evapotranspiration

	Compton		Porton	
Parameter	Concentration or value	Concentrated rainfall	Concentration or value	Concentrated rainfall
pH	5.46		6.04	
SEC (μS cm^{-1})	25.8	77.4	33.3	99.9
Na (mg L^{-1})	1.30	3.91	2.16	6.48
K (mg L^{-1})	0.365	1.09	0.367	1.10
Ca (mg L^{-1})	0.734	2.20	(14.5)	
Mg (mg L^{-1})	0.168	0.504	0.349	1.04
Cl (mg L^{-1})	2.33	6.99	3.67	11.0
SO_4 (mg L^{-1})	2.55	7.65	2.22	6.66
NO_3-N (mg L^{-1})	0.561	4.05*	0.483	2.90*
NH_4-N (mg L^{-1})	0.791		0.483	

* assuming all NH_4 oxidises to NO_3-N

3.4 RAINFALL CHEMISTRY

Rainfall is the primary source of recharge to the Chalk and a primary source of many solutes. The mean rainfall compositions for the closest national monitoring stations (Compton and Porton) are shown in Table 3.1. The composition of recharge will be modified by processes such as mineral dissolution (e.g. Ca, K, Mg) and further modified by uptake of plant nutrients (e.g. K and N) but the rainfall data provide an estimate of initial inputs against which to compare groundwater composition. Chloride is assumed to behave conservatively during recharge, which would suggest that concentrations in infiltrating waters unaffected by other sources of chloride should have initial concentrations of around 2–4 mg L^{-1}, with some variation likely due to distance from the coast.

Edmunds et al. (1987) investigated the rainfall chemistry of sites on the Chalk of Berkshire and compared the solute concentrations with those from unsaturated porewaters in the same area. The results from Cl data suggested concentration factors of around 2–5 for the interstitial waters, an increase that was likely to be predominantly due to evaporation. This range compares with a factor of 3.8 determined for groundwaters in the Netherlands (Appelo and Postma, 1993). The effect of evapotranspiration on the chemistry of infiltrating recharge are notoriously difficult to quantify, but as an estimate a concentration factor of three has been used as an approximation. This suggests that recharge having undergone evapotranspiration should have Cl concentrations in the region of 7–11 mg L^{-1}. Assuming all NH_4 oxidises to NO_3 during recharge (which may or may not be realistic), total N concentrations in recharge water of around 3–4 mg L^{-1} would be expected.

3.5 CURRENT ISSUES IN GROUNDWATER QUALITY

The Environment Agency Draft River Basin Management Plan for the South East River Basin District (EA, 2008) assesses the current status of groundwater quality in the study area as poor. The risks of not achieving quality objectives by 2015 under the Water Framework Directive are as follows:

- at risk for nitrate due to trends of increasing concentration in groundwater from both the Test and Itchen catchments;

- probably at risk for sheep dip and pesticides;
- not at risk for phosphate, priority hazardous substances, chlorinated solvents.

Issues over the whole area which were assessed as not being significant were faecal indicator organisms, mines and minewaters, metals, endocrine disruptors.

4 Data availability and analytical methodology

4.1 ARCHIVE GROUNDWATER DATA SOURCES

Groundwater chemistry data for the study area were compiled from a number of sources. These included available analyses from the Environment Agency groundwater-monitoring network which were reported as part of a study of the Chalk aquifer of the Wessex Basin (Allen et al., 2009). Data for a few boreholes that were out of service at the time of that survey were provided by the relevant water utility. In these cases, a recent sample with the maximum number of analytes was selected. Data were also included from an investigation of groundwater from pumping stations at Lower Upham, Hoe, and Newtown, reported by Darling et al. (2005).

Details of porewater chemistry data for the area are also available from Young et al. (1976), Kinniburgh and Trafford (1995) and Stuart et al. (2008a).

4.2 GROUNDWATER SAMPLING AND ANALYSIS

A new groundwater sampling campaign was also carried out for this study. A total of 27 water samples were collected by BGS during November 2007 and January 2008. Sampling sites were selected to give a good spatial coverage of the area and to represent north-south flow lines across the aquifer.

Sampling included on-site measurements of temperature, specific electrical conductance (SEC), alkalinity, pH, dissolved oxygen (DO) and redox potential (Eh). Alkalinity was measured by titration against H_2SO_4 and is reported as HCO_3. Where possible, the pH, Eh and DO were measured in a flow cell to restrict aeration and were monitored until stable readings were obtained.

Where possible, samples were collected from boreholes that were in regular or continuous use. In cases where borehole pumps had to be switched on specifically for the sampling, a minimum purging time equivalent to around two borehole volumes was allowed prior to sampling. Where this was not possible due to lack of accommodation of the volume of discharge, on-site parameters were monitored to ensure that readings had stabilised.

At each site, samples for the analysis of major and trace elements were collected in polyethylene (Nalgene®) bottles. All samples were filtered through a 0.45 μm filter and aliquots for cation and trace-element analysis were acidified to 1% v/v HNO_3 to prevent metal precipitation and to minimise adsorption onto container walls. Samples for analysis of total dissolved phosphorus (TDP) were collected in 60 mL polyethylene bottles preloaded with potassium persulphate. Samples for dissolved organic carbon (DOC) were filtered through a 0.45 μm silver-impregnated filter and collected in chromic-acid-washed glass vials. Samples for the determination of stable isotopes (O, H, and C) were collected unfiltered into glass bottles. At suitable sites, samples were collected for the measurement of the atmospheric trace gases CFC and SF_6 following the displacement method described in (Oster et al., 1996). These samples were unfiltered and were collected in glass bottles contained within metal cans to avoid atmospheric contact and to ensure that the sample is protected from atmospheric contamination by a jacket of the same water.

Major cations and sulphate were measured by inductively-coupled plasma optical-emission spectrometry (ICP-OES) and anion species by ion chromatography (Cl, Br, F) or automated colorimetry (NO_2-N, NH_4-N, I), all at the BGS laboratory in Wallingford. In addition, a wide range of trace elements was analysed by inductively-coupled plasma mass spectrometry (ICP-

Figure 4.1 On-site measurement of unstable parameters at a water utility sampling point

MS) at the BGS laboratory, Keyworth. Analysis of TDP was by sample digestion followed by colorimetry using the molybdenum blue method. Sample preparation and analysis was carried out by CEH at the Wallingford laboratory.

Ionic balances for the analyses were within ± 4%. The precision of the trace-element data was verified by determining the relative standard deviation (rsd) of replicate analyses. The median rsd for all elements is < 1% although somewhat higher rsd values (max 35%) are observed where elemental concentrations lie near the detection limit.

4.3 DATA HANDLING

Available data from the sampling survey and previous studies were collated for the determination of statistical summaries and subsequent interpretation. Many of the trace elements in the dataset were below analytical detection limits and a rigorous approach to computation of statistical distributions was therefore required. Summary statistics were calculated using R (R Development Core Team, 2005) with the NADA package (USGS, 2008). NADA is specifically designed for the statistical treatment of multiply censored (non-detect) environmental data and contains the analysis methods described in Helsel (2005).

The procedures applied in this study for estimating summary statistics include the non-parametric Kaplan-Meier (K-M) method and the robust ROS (Regression on Order Statistics) method. Summary statistics were also calculated using maximum likelihood estimation (MLE) but have not been reported in this study as the method does not perform well for datasets with less than around 50 observations (Shumway et al., 2002; Helsel, 2005). Indeed, our computations indicated systematically higher values for statistical parameters based on MLE compared with statistical summary data computed by K-M or robust ROS.

Table 4.1 Methods for calculating summary statistics for individual trace elements where populations include censored data (for elements with >80% non-detects; only ranges are computed).

Element/ion	Method	Element/ion	Method
NO_2 as N	ROS	Hf	ROS
NH_4 as N	ROS	Li	K-M
P	K-M	Mn	ROS
DOC	K-M	Mo	K-M
F	K-M	Ni	K-M
Br	K-M	Pb	K-M
I	K-M	Rb	K-M
Si	K-M	Sb	K-M
Al	ROS	Se	ROS
As	ROS	Sr	K-M
Ba	K-M	Tl	K-M
Ce	ROS	U	K-M
Co	K-M	V	K-M
Cr	K-M	Zn	K-M
Cu	K-M		

The Kaplan-Meier (K-M) method is used for survival analysis in the medical sciences, but is also applicable for environmental data. The method is particularly useful for summarising censored environmental data as it does not make or require an assumption about the underlying distribution of the data and does not require estimates of the unknown distance between non-detects and detected values, only their relative order (Helsel, 2005). The Kaplan-Meier method calculates the relative position (rank) of the observed data and computes summary statistics based on the survival probability function for right-censored, i.e. above-detection-limit, data. For environmental applications where data are more typically left-censored, it is necessary to 'flip' the data, or subtract the measurements from a constant value which exceeds that of the data range. This procedure effectively converts left-censored to right-censored data. Once data have been flipped, the mechanics of the Kaplan-Meier method are identical to those used for medical survival data. After computation, the data are reconverted to the original scale. The Kaplan-Meier method is considered suitable for data sets with varying numbers of observations, provided that less than 50% of the data are censored (Helsel, 2005). Where censoring is greater than 50% and the smallest observation is a non-detect, the method cannot return a median value. Where censoring is greater than 50%, estimation of statistical parameters including percentiles is best achieved using alternative methods such as robust ROS (or for large datasets MLE) (Lee and Helsel, 2005).

The robust ROS method (termed MR, Multiple-limit Regression (MR) by Helsel and Cohn, 1988) calculates a statistical distribution using a linear regression based on actual observations for non-censored data and assuming a distribution for censored data. The method (as used in NADA (USGS, 2008)) first computes the Weibull plotting positions of the combined censored and non-censored dataset and performs a linear regression using the plotting positions of the uncensored observations and their normal quantiles. This is then used to predict the concentration of the censored observations as a function of their normal quantiles. Summary statistics for the population are computed on the basis of the combined observed and modelled values. The method is suited for small data sets of say <30–50 observations, where MLE estimations of statistical parameters become inaccurate, and for datasets with a large proportion of censored observations (Helsel, 2005). It is also considered one of the most reliable procedures for estimating summary statistics of multiply-censored data (Shumway et al., 2002).

Summary statistics for individual determinands considered in this study were calculated using the recommendations of Helsel (2005):

Non-detects <50%	K-M method
Non-detects >50% and <80%	robust ROS method
Non-detects >80%	ranges only.

Consequently, different procedures were used for calculating the summary statistics of the different determinands and the methods applied for each are detailed in Table 4.1. Statistical summaries for the major ions were all calculated using the Kaplan-Meier method. Computed data include the 5, 25, 50, 75, 90 and 95th percentiles, together with the mean, observed minimum, observed maximum, number of observations and number of censored observations. As chemical analytes in groundwater, particularly trace elements, are rarely normally distributed, simple observed maxima, minima and arithmetic means are often not the best ways of summarising data distributions. The median (50th percentile) is considered a better indicator of central tendency than the mean because of its reduced sensitivity to skewed data and outliers.

As a result of often skewed distributions, use of cut-off points to exclude extremes and outliers has often been used to try to define an upper limit, or threshold, on baseline concentrations in a given system (Edmunds et al., 1997; Kunkel et al., 2004; Sinclair, 1974). Various upper percentiles have been used in the literature for this purpose, e.g. 90th–95th (Lee and Helsel, 2005) or 98th (Langmuir, 1997) percentile. The choice of percentile is inevitably somewhat arbitrary. For many determinands in this study, the 95th percentile has been taken as a cut-off to eliminate upper outliers and provide a first approximation to 'upper baseline' concentrations. Care needs to be taken with this approach: for example, groundwater in most aquifers in the UK is impacted by inputs of nitrate from agricultural or domestic sources. Thus, an upper baseline estimate would likely be much lower than the 95th percentile for most groundwater nitrate datasets. Similarly, data above the 95th percentile could in some circumstances represent baseline compositions if concentrations of determinands in baseline and non-baseline populations overlap significantly (Sinclair, 1974). Nevertheless, the 95th percentile by definition represents the concentration that is exceeded by only 5% of the observations and is unlikely to be exceeded unless conditions in the aquifer have changed.

Chemical data are presented in summary statistical tables and data for major ions and selected trace elements are presented as box plots and cumulative probability diagrams. Graphical outputs have been plotted using the NADA package in R. In the box plots, boxes represent the interquartile range with the median given as a horizontal white line. Box plot whiskers are equal to no more than 1.5 times the interquartile range of the distribution. Box plots for determinands with censored data have been constructed using the robust ROS method. Outliers are given as circles beyond the whisker range. Box plot widths are proportional to the square root of the number of observations.

Cumulative probability distributions of solutes have been constructed by computing the empirical cumulative distribution function for censored data using the Kaplan-Meier method. This has been plotted on a probability scale against log concentration values. Applications of the cumulative-probability diagram have been described in detail by Sinclair (1974), Reimann and Garrett (2005) and Reimann et al. (2008).

5 Regional hydrogeochemistry

5.1 MAJOR CONSTITUENTS

Statistical data for major ions, field-determined parameters and stable isotopes used in the present study are summarised in Table 5.1. The sampled groundwaters generally display a relatively narrow range of physico-chemical characteristics and solute concentrations.

Temperatures of the newly sampled groundwaters ranged from 10.1 to 11.5°C. A number of values from previous surveys were higher, reaching up to 15.5°C. The overall median was 10.7°C. Lowest values were mainly found in boreholes close to the groundwater divide, perhaps reflecting recent recharge. Some of the higher values were found in groundwaters below the Palaeogene cover in the south.

The measurements of dissolved-oxygen concentration (DO) and redox potential (Eh) indicated that all the groundwaters sampled were oxidising with DO ranging upwards from 4.5 mg L^{-1} to near-saturated and Eh from 340 to 440 mV. The lowest Eh values were observed in boreholes which had not been pumped regularly prior to the survey. These included a river augmentation borehole and a trial public-supply borehole.

The small pH range and near-neutral values (median pH 7.11) are all consistent with groundwater being well-buffered by carbonate equilibrium reactions. A Piper plot (Figure 5.1) confirms that groundwaters in the unconfined Hampshire Chalk have little variation in major-ion composition and are of Ca-HCO_3 type, as is typical of such Chalk groundwaters.

The groundwaters are weakly mineralised with specific electrical conductance (SEC) ranging from 466 to 715 µS cm^{-1} and with a median value of 565 µS cm^{-1}. The highest values were found in the Basingstoke urban area and from Chalk below the Palaeogene cover at Timsbury.

Table 5.1 Statistical summary of field-determined parameters, major ions, nitrogen species and stable-isotopic compositions of groundwaters from the Hampshire Chalk aquifer

Parameter	Units	n	n (c)	Min	Mean	Max	P5	P25	P50	P75	P90	P95
Temp	°C	31	0	10.1	11	15.5	10.1	10.3	10.7	11.1	11.5	12.8
pH		37	0	6.88	7.14	7.55	6.9	7.04	7.11	7.19	7.4	7.5
Eh	mV	23	0	340	407	440	343	400	415	426	433	435
DO	mg L^{-1}	30	0	4.5	7.68	10.6	4.68	6.62	7.75	8.74	9.6	10.4
SEC	µS cm^{-1}	37	0	466	563	715	467	532	565	581	638	690
δ^2H	‰	19	0	-46.1	-43.3	-40.4	-45.9	-44.7	-43.6	-41.9	-41.1	-40.8
$\delta^{18}O$	‰	19	0	-7.32	-6.84	-6.18	-7.3	-7.14	-6.89	-6.7	-6.31	-6.28
$\delta^{13}C$	‰	3	0	-15.5	-10.1	0.19	-15.4	-15.2	-15	-7.4	-2.84	-1.33
Ca	mg L^{-1}	36	0	94.4	109	144	97.2	102	105	113	121	123
Mg	mg L^{-1}	36	0	1.4	2.1	4.81	1.51	1.83	1.98	2.15	2.41	3.74
Na	mg L^{-1}	37	0	5.45	8.88	14.4	6.13	7.66	8.61	10.3	11.6	12.5
K	mg L^{-1}	37	1	<0.5	1.47	3.53	0.59	1.08	1.33	1.63	2.51	2.96
Cl	mg L^{-1}	37	0	11.8	17.7	26.3	12.9	15.6	17.7	19.3	21.9	23.5
SO_4	mg L^{-1}	36	0	4.73	12.9	22.8	7.56	10.7	11.8	14.7	18.4	19.2
HCO_3	mg L^{-1}	36	0	254	292	355	260	274	286	307	318	347
NO_3-N	mg L^{-1}	37	1	<0.05	6.58	12.6	2.68	5.72	6.53	7.33	8.99	10.7
NO_2-N	mg L^{-1}	36	24	<0.0006	0.0017	0.010	0.0001	0.0003	0.0005	0.0017	0.0048	0.0080
NH_4-N	mg L^{-1}	37	29	<0.005	0.00917	0.066	0.0001	0.0005	0.0012	0.0051	0.0336	0.0637
DOC	mg L^{-1}	27	0	0.46	0.813	1.24	0.58	0.7	0.8	0.91	1.0	1.1
Si	mg L^{-1}	35	0	4.57	5.73	9.37	4.79	5.21	5.57	6.03	6.71	7.34

DO: dissolved oxygen; P = percentile; n (c) = number censored; min and max are observed values

The major-ion data are shown as box plots in Figure 5.2. These also indicate the limited ranges of major-ion concentrations, with the exception of NO_3-N which had one sample below the detection limit of 0.05 mg L^{-1}.

Cumulative-probability distributions for major ions are shown in Figure 5.3. These also illustrate the distribution, range and relative abundance of solutes in groundwater and are useful tools for visualising data. Many show near straight-line distributions (log scale) although some apparent upper outliers are seen for Mg, K and NO_3-N and, as with the box plot, a prominent lower tail is seen in the NO_3-N distribution.

The concentrations of Ca and HCO_3 are an order of magnitude higher than the other major ions and have a proportionately narrower range of distribution. The narrow range of concentrations for Ca (94–144 mg L^{-1}) and the linear cumulative-probability curves indicate the rapid solution of calcite to its solubility limit. Some sources in the Meon catchment (together with Avington, Ibthorpe and Chilbolton) are slightly undersaturated with respect to calcite.

Measured Cl concentrations have a 5–95 percentile range of 12.9–23.5 mg L^{-1}, with a median of 18 mg L^{-1}. The range is slightly enriched compared to Cl estimated for rainfall-derived local recharge (11 mg L^{-1}; Table 3.1). Chloride concentrations appear to have no obvious spatial trend (Appendix 1, Plate 2) although one sample from Chalk below the Palaeogene cover had a relatively high concentration (22.5 mg L^{-1}). Urban pollution may have had a minor impact on concentrations (e.g. around Basingstoke; Appendix 1, Plate 2), but there is little evidence for this from the cumulative-probability curve (Figure 5.3) which is near-linear and does not indicate the presence of mixed sample populations. A similar probability distribution is shown for Na (Figure 5.3) which has a median value of 8.6 mg L^{-1} and a 5–95 percentile range of 6.1–12.5 mg L^{-1}. These values compare reasonably well with an estimate for local recharge water of around 6.5 mg L^{-1} (Section 3.4).

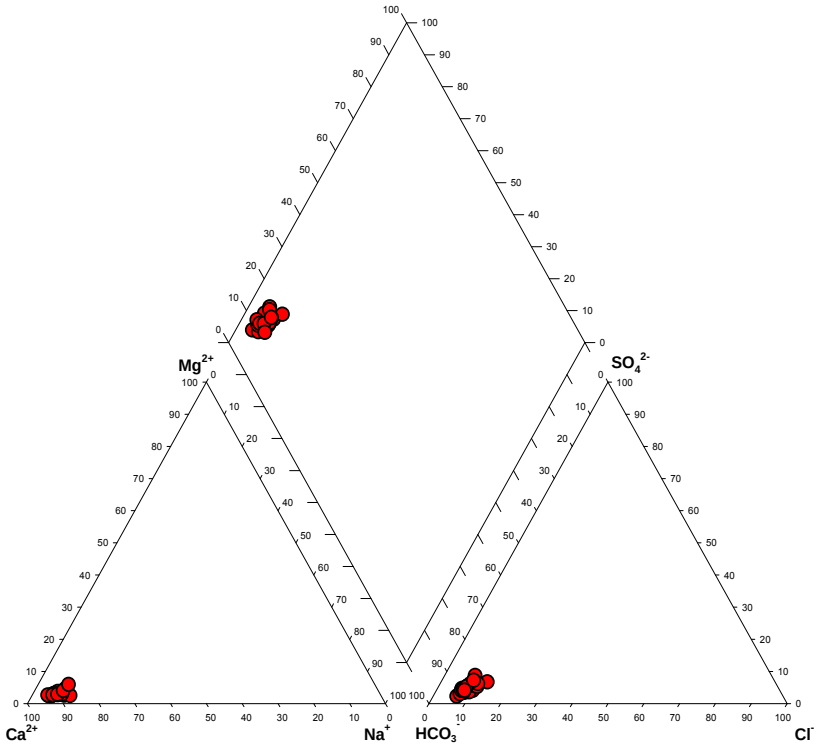

Figure 5.1 Piper plot of major ions in groundwater in the Hampshire Chalk aquifer

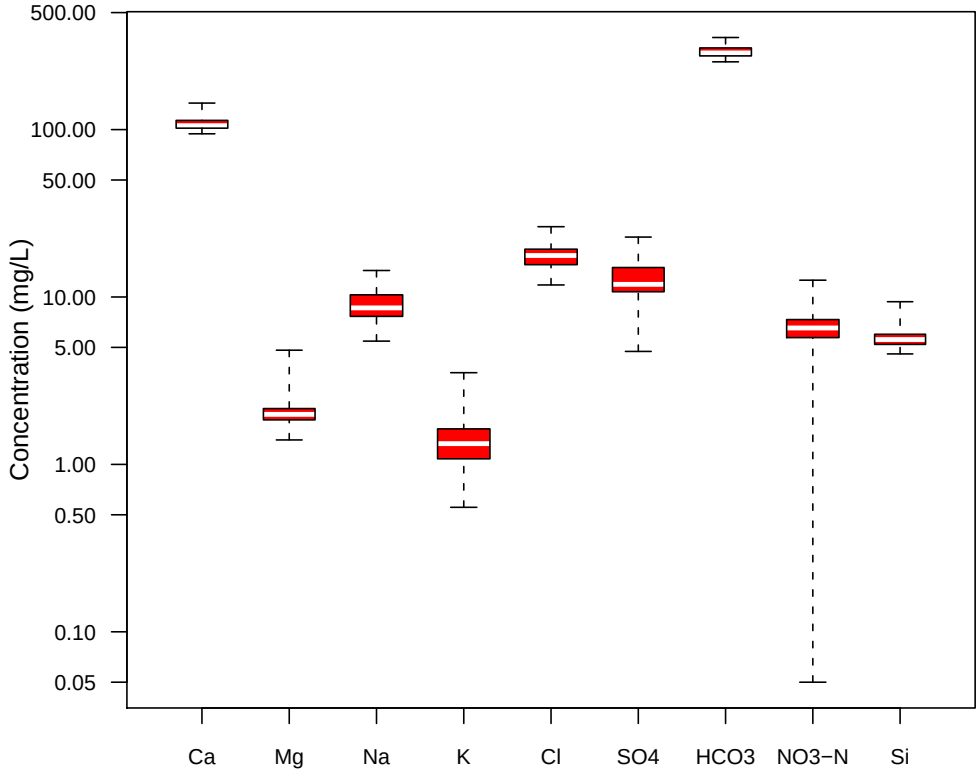

Figure 5.2 Box plots for the major ions in groundwater in the Hampshire Chalk aquifer

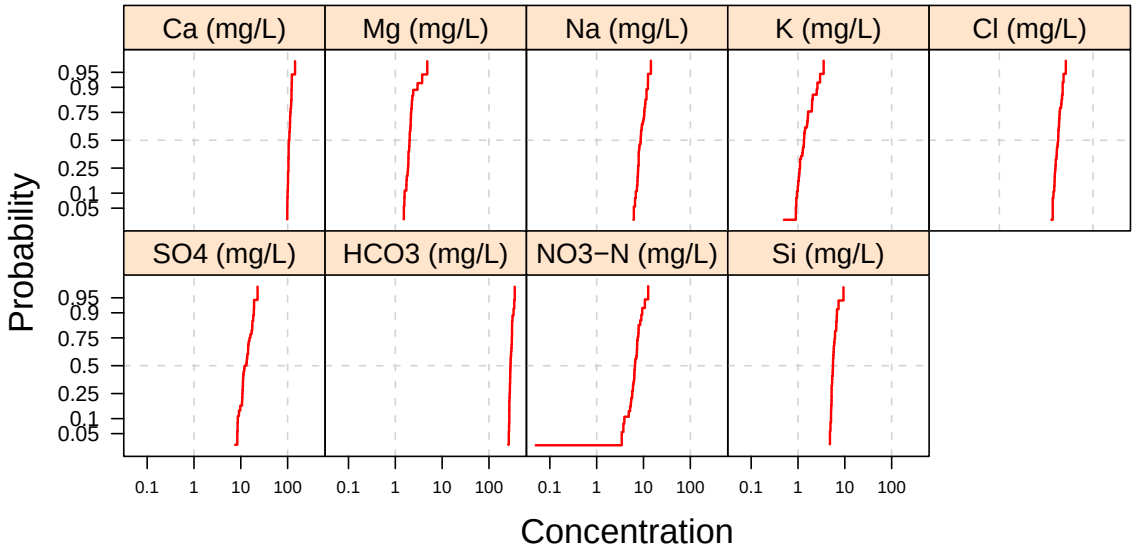

Figure 5.3 Cumulative probability plots for major ions in the Hampshire Chalk aquifer

Magnesium concentrations are low (median 1.98 mg L^{-1}), as expected for unconfined Chalk groundwaters. However, they show a slight positive deviation above about 3 mg L^{-1} (probability 0.9; Figure 5.3) due to the influence of a small number of samples from beneath the Palaeogene cover. The Mg in these samples most likely reflects inputs from reactions with clay minerals in the Palaeogene strata. Nonetheless, the magnitude of the increase in these samples is small, only of the order of 1 mg L^{-1}.

Concentrations of K range from below the detection limit to 3.53 mg L^{-1} with a median value of 1.33 mg L^{-1}. Some of the lowest concentrations occur in the central part of the study area, perhaps reflecting proximity to the groundwater divide. One sample (from Chilbolton) had a concentration below the detection limit of 0.5 mg L^{-1}. The highest concentration was from a borehole below the Palaeogene in the south-west of the area. As with Mg, the concentration of K in this sample may have been increased as a result of reactions with clay minerals in the overlying Palaeogene sediments. Potassium may also be derived from reaction with clay minerals in the Chalk. Pollution from fertilisers may be an additional source.

Sulphate concentrations are low (median 11.8 mg L^{-1}) and are similar to concentrations found in the Dorset Chalk (Shand et al., 2007). One very low value occurs close to the groundwater divide at Dummer [SU 591 465]. Sulphate is likely to be derived largely from atmospheric inputs, although additional sources such as pyrite may be involved. Pyrite is known to be present in hardgrounds in the Chalk and is likely also to be present in the Palaeogene deposits. Some of the highest concentrations are found in the groundwaters below the Palaeogene (Appendix 1, Plate 4), likely reflecting inputs from oxidised pyrite during infiltration of recharge via the Palaeogene cover.

Nitrate has a median value of 6.5 mg L^{-1} as N. This compares reasonably well with concentrations in other unconfined groundwaters from the Chalk (Shand et al., 2007), although the observed range is in excess of concentrations estimated from local recharge (3–4 mg L^{-1}; Table 3.1). One sample had a concentration above the national/European drinking-water limit (11.3 mg L^{-1} N). Distributions of nitrate tend to be slightly higher in the Test and Loddon catchments in the northern and western parts of the study area compared to the Itchen catchment to the east (Appendix 1, Plate 4). The highest observed concentrations are likely to be related to land-use with inputs from fertilisers and to a lesser extent from point sources. As noted above, one sample had a concentration below the detection limit. This sample also had relatively high concentrations of Na (14.4 mg L^{-1}), P (193 µg L^{-1}) and Pb (1.35 µg L^{-1}) and an Eh value at the lower end of the observed range. Nonetheless, concentrations of Fe and Mn were relatively low and indicative of oxic conditions with respect to these elements. The sample was from one of the sources that had not been pumping for a while before sampling and may have been subject to mild reduction of NO_3 in the vicinity of the borehole.

Concentrations of NO_2-N and NH_4-N were uniformly low and below the limit of detection over most of the area. Observed maxima were 0.01 mg L^{-1} for NO_2-N and 0.066 mg L^{-1} for NH_4-N. Samples with detectable concentrations tended to be grouped in the south-east, in the Meon valley and north of Winchester and in the north at Kingsclere (Appendix 1, Plate 4). Both species can be indicators of pollution (fertilisers, slurry or domestic waste), although they can also be of natural origin: nitrite is produced as an intermediary meta-stable species during denitrification in soils and aquifers and ammonium is stable under strongly reducing conditions as a result of degradation of organic matter. Anthropogenic inputs may be partially responsible for the detectable concentrations of these species in the Hampshire groundwaters, although the scale of such inputs is minor.

Dissolved organic carbon (DOC) concentrations are also low (median 0.8 mg L^{-1}) and are similar to those observed in the Dorset Chalk (Edmunds et al., 2002). DOC is generally derived from soil reactions but can also be enhanced by inputs from pollution sources (e.g. slurry pits, landfills). In this study, the lowest values were recorded at sites where the borehole was switched on and pumped specifically in order to collect and sample. As with the low-nitrate source, these may contain a component of static water which has not been fully flushed from the system.

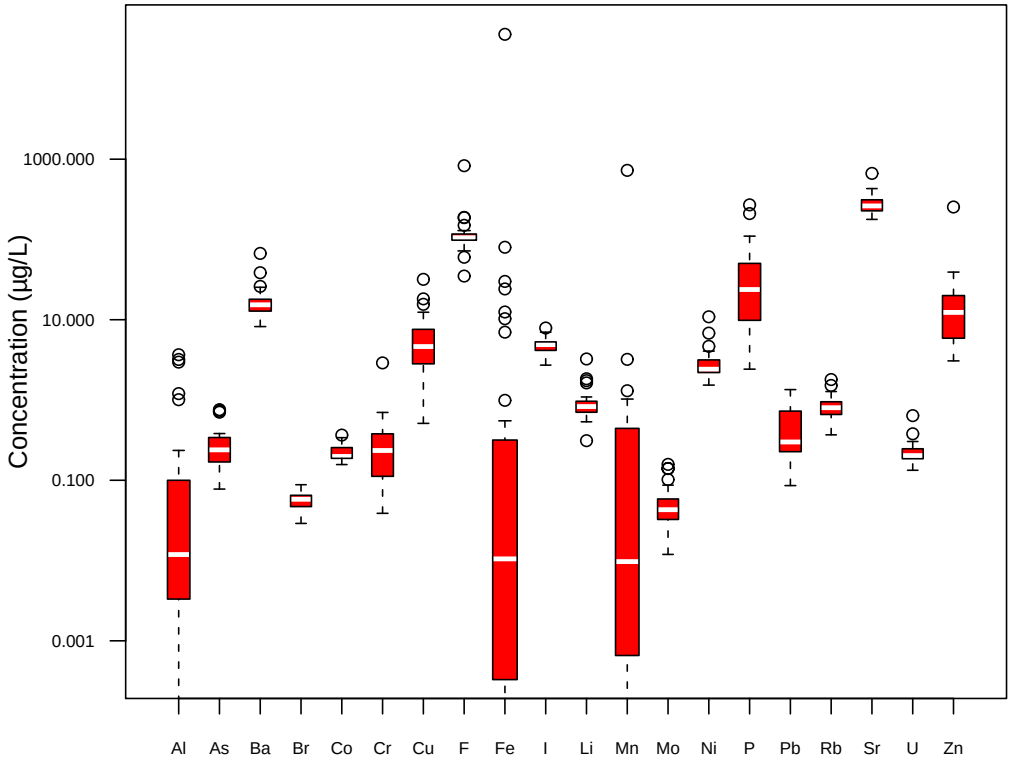

Figure 5.4 Box plots for trace elements in groundwater in the Hampshire Chalk aquifer

Silicon concentrations are relatively uniform, ranging from 4.6 to 9.4 mg L^{-1} (5-95 percentile range 4.8–7.3 mg L^{-1}). Higher concentrations are observed in the eastern part of the area with the greatest values at Kingsclere and Lasham, close to the outcrop of the Upper Greensand. These boreholes penetrate to the Lower Chalk but do not reach the Upper Greensand so the source of Si in Chalk groundwater is likely to be clay minerals or flint within the Chalk matrix.

5.2 TRACE ELEMENTS

Data for minor and trace elements in the groundwaters are summarised in Table 5.2 and in Figure 5.4 and Figure 5.5.

5.2.1 Phosphorus

Concentrations of total dissolved phosphorus vary widely over the area with a 5–95 percentile range of 10–193 µg L^{-1} and median of 19 µg L^{-1}. The cumulative-probability plot is non-linear (Figure 5.5) with an apparent break in slope at around 80 µg L^{-1}. The highest concentrations are observed in the Alresford and Candover area (Appendix 1, Plate 5). Dissolved P concentrations in groundwater can be derived from both natural and anthropogenic sources. In the Chalk groundwaters, likely mineral sources include phosphate minerals, especially in hardgrounds, and potentially also exchangeable P from iron oxides. However, other sources can include inorganic and organic fertilisers, effluent from water treatment and farmyard slurry. There is no apparent correlation between P and other potential indicators of agricultural/domestic pollution such as NO_3 or DOC.

Table 5.2 Statistical summary of trace elements in groundwaters from the Hampshire Chalk aquifer

Element	Units	n	n (c)	Min	Mean	Max	P5	P25	P50	P75	P90	P95
Ag	µg L^{-1}	28	27	<0.1		0.023						
Al	µg L^{-1}	32	25	<5	0.416	3.67	0.0003	0.00331	0.0119	0.100	1.20	3.08
As	µg L^{-1}	29	16	<0.4	0.302	0.757	0.102	0.169	0.239	0.341	0.708	0.737
B	µg L^{-1}	37	36	<40		28						
Ba	µg L^{-1}	31	1	8.22	18.3	67.7	9.49	13.4	15.1	18.0	25.4	38.5
Be	µg L^{-1}	27	27	<0.2		<0.2						
Bi	µg L^{-1}	3	3	<0.05		<0.05						
Br	µg L^{-1}	27	0	29	56	88	35	45	58	67	73	73
Cd	µg L^{-1}	34	28	<0.5	0.089	2.44						
Ce	µg L^{-1}	27	26	<0.005	0.00278	0.01						
Co	µg L^{-1}	27	0	0.157	0.226	0.365	0.163	0.187	0.198	0.262	0.337	0.340
Cr	µg L^{-1}	29	8	<0.6	0.355	2.90		0.112	0.235	0.379	0.505	0.700
Cs	µg L^{-1}	27	27	<0.02		<0.02						
Cu	µg L^{-1}	29	1	<10	6.68	31.8	1.29	2.56	4.63	7.59	15.6	18.2
Dy	µg L^{-1}	24	24	<0.005		<0.005						
Er	µg L^{-1}	24	24	<0.005		<0.005						
Eu	µg L^{-1}	24	24	<0.005		<0.005						
F	µg L^{-1}	37	0	35	126	830	60	98	105	117	150	188
Fe	µg L^{-1}	37	30	<5		36000						
Ga	µg L^{-1}	24	24	<0.1		<0.1						
Gd	µg L^{-1}	24	24	<0.005		<0.005						
Ge	µg L^{-1}	24	24	<0.3		<0.3						
Hf	µg L^{-1}	24	18	<0.005	0.0052	0.0390	0.0002	0.0008	0.002	0.005	0.013	0.014
Hg	µg L^{-1}	2	2	<0.005		<0.005						
Ho	µg L^{-1}	27	27	<0.005		<0.005						
I	µg L^{-1}	27	0	2.72	4.88	7.9		4.1	4.9	5.3	6.1	7
La	µg L^{-1}	27	25	<0.005		0.006						
Li	µg L^{-1}	27	0	0.311	0.964	3.25	0.535	0.669	0.829	0.994	1.74	1.84
Lu	µg L^{-1}	24	24	<0.005		<0.005						
Mn	µg L^{-1}	34	25	<0.3	21	726	0.00003	0.00075	0.00971	0.411	0.99	1.97
Mo	µg L^{-1}	27	3	<0.02	0.055	0.158		0.032	0.043	0.06	0.14	0.14
Nb	µg L^{-1}	24	24	<0.01		<0.01						
Nd	µg L^{-1}	27	26	<0.005		0.013						
Ni	µg L^{-1}	29	0	1.53	3.04	10.9	1.69	2.20	2.42	3.16	4.66	6.80
P	µg L^{-1}	27	0	9	40	308	10	11	19	30	60	193
Pb	µg L^{-1}	29	1	<1	0.447	1.35	0.087	0.200	0.299	0.727	0.874	1.09
Pr	µg L^{-1}	24	24	<0.005		<0.005						
Rb	µg L^{-1}	27	0	0.368	0.867	1.80	0.442	0.638	0.802	0.979	1.27	1.52
Sb	µg L^{-1}	29	2	<0.1	0.042	0.073	0.018	0.032	0.0397	0.052	0.067	0.0687
Se	µg L^{-1}	30	24	<0.8	1.42	30.0	0.0014	0.0129	0.0622	0.381	2.05	2.58
Sm	µg L^{-1}	24	24	<0.005		<0.005						
Sn	µg L^{-1}	27	26	<0.2		0.506						
Sr	µg L^{-1}	27	0	178	289	664	199	225	262	319	423	430
Ta	µg L^{-1}	24	24	<0.005		<0.005						
Tb	µg L^{-1}	24	24	<0.005		<0.005						
Th	µg L^{-1}	27	23	<0.02		0.084						
Tl	µg L^{-1}	27	2	<0.005	0.01	0.040		0.007	0.01	0.013	0.017	0.020
Tm	µg L^{-1}	24	24	<0.005		<0.005						
U	µg L^{-1}	27	0	0.133	0.232	0.639	0.159	0.183	0.203	0.247	0.304	0.380
V	µg L^{-1}	27	0	0.148	0.284	0.480	0.162	0.229	0.284	0.337	0.387	0.412
W	µg L^{-1}	24	22	<0.005		0.014						
Y	µg L^{-1}	27	25	<0.01		0.0144						
Yb	µg L^{-1}	24	24	<0.005		<0.005						
Zn	µg L^{-1}	30	0	3.07	21.8	253	3.25	5.88	11.5	20.0	25.6	39.2
Zr	µg L^{-1}	27	23	<0.01		0.032						

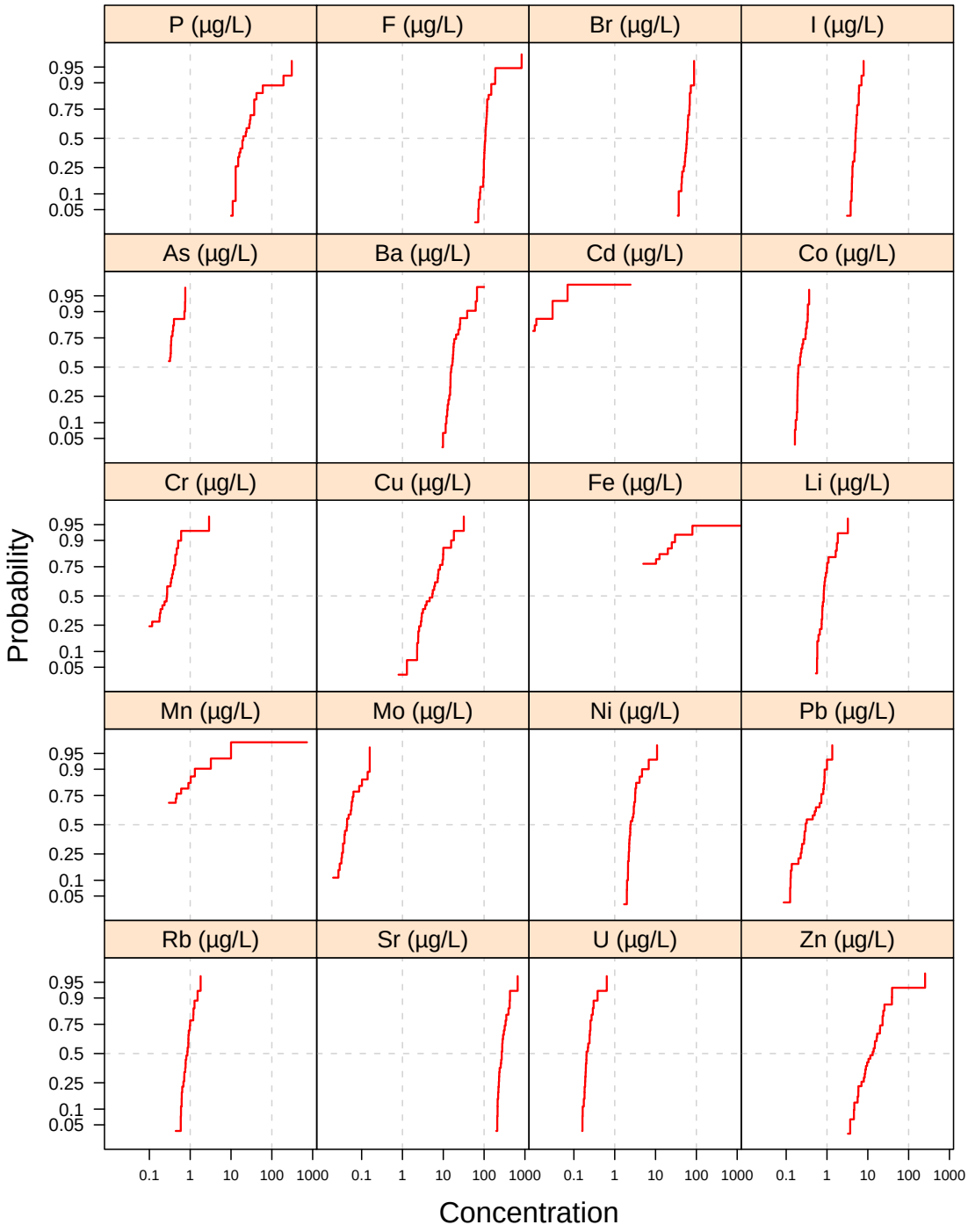

Figure 5.5 Cumulative-probability plots for selected trace elements in groundwater from the Hampshire Chalk aquifer

5.2.2 Halogen elements

Concentrations of F are generally low (median 105 µg L^{-1}) with the highest values observed in groundwaters from below the Palaeogene cover in the south of the area. As with P, the most likely source of F in the groundwaters is phosphate minerals (including fluorapatite). These are present in hardgrounds and marl horizons within the Chalk. Adsorbed P on iron oxides represents a possible additional source in the Palaeogene sediments (sands and clays)

above the Chalk. Concentrations of dissolved F in the Chalk groundwaters are generally low because of the presence of dissolved Ca as the dominant cation.

Concentrations of Br are lowest along the groundwater divide and higher in the downgradient sections, both close to and below the Palaeogene deposits. The log probability distribution is near-linear with no apparent outliers. The Br/Cl ratio shows a similar north to south increase, being lowest at Axford and highest at Timsbury, Soberton West Street and Chilbolton.

Concentrations of I (median 4.88 μg L^{-1}) are also lowest in the central part of the study area near the groundwater divide (Plate 5). As with Br, the groundwaters have a narrow range of concentrations and a near-linear log probability distribution.

5.2.3 Alkaline earth elements

Barium has a relatively narrow range of concentrations with a median of 15 μg L^{-1} and a 5–95 percentile range of 9.5–38.5 μg L^{-1}. A slight break in slope is seen in the log probability distribution at around 30 μg L^{-1}. Two samples had Ba concentrations greater than 30 μg L^{-1} with the observed maximum being 67 μg L^{-1}. Both were from Chalk groundwater below Palaeogene deposits (Plate 4) and the increased concentrations most likely derive from reactions of groundwater with clay minerals and possibly feldspars in these overlying deposits. Detrital barite represents a possible additional source of Ba. All samples were undersaturated with respect to barite as a result of the low concentrations of dissolved SO_4 present.

Strontium has a median concentration of 262 μg L^{-1}, a value typical for unconfined Chalk groundwater. As with many other trace elements, concentrations are highest both close to and below the Palaeogene cover (Plate 4). The lowest concentrations occur at the groundwater divide around Overton, Andover, St Mary Bourne, Whitchurch and Dummer. Highest occur at West Ham Park, Woodgarston and Kingsclere in the north-west and Soberton in the south, as well as below the Palaeogene cover at Timsbury and Newtown. As Sr has similar geochemical behaviour to Ca, it can reasonably be expected to derive from similar sources, principal being dissolution (and diagenesis) of the Chalk. Strontium is released from marine carbonates during incongruent dissolution and therefore increasing Sr concentrations and Sr/Ca ratios can be an indication of increasing groundwater residence time (e.g. Edmunds and Smedley, 2000). Some inputs of Sr from the clays in the Palaeogene strata are also indicated by the relatively high values in these samples.

5.2.4 Alkali metals

Lithium concentrations have a 5–95 percentile range of 0.54–1.84 μg L^{-1} and a median of 0.83 μg L^{-1}. The range is very similar to that observed in the unconfined Dorset Chalk. The highest concentration (3.3 μg L^{-1}) was from a borehole at Kingsclere on the northern edge of the outcrop. Lithium data are only available for one sample from Chalk beneath Palaeogene cover. This sample had a relatively high concentration (95 percentile 1.84 μg L^{-1}) and it is likely that a component of this is derived from clay minerals in the Palaeogene sands and clays.

Rubidium concentrations have a narrow range with an observed median of 0.8 μg L^{-1} (Figure 5.5). As with Li, the sample with the highest observed concentration (1.8 μg L^{-1}) was derived from Chalk below the Palaeogene. The most likely source of Rb is clay minerals in the Chalk (notably hardgrounds and marls) or the Palaeogene silicate sediments. Alkali feldspar represents a possible additional, though less abundant, source.

5.2.5 Arsenic and selenium

Arsenic concentrations were low in all samples with a median value of 0.24 μg L^{-1} and a 5–95 percentile range of 0.10–0.74 μg L^{-1}. All observations, including those from below the Palaeogene cover, were <1 μg L^{-1}. Such low concentrations are expected under oxic conditions in a Chalk (neutral-pH) aquifer.

Selenium also has usually low concentrations, most being below detection limits and all but six samples having <1 μg L^{-1}. The maximum observed concentrations was 30 μg L^{-1}. This, together with several observations greater than 1 μg L^{-1}, was from Chalk below Palaeogene cover. This strongly suggests derivation of Se from overlying Palaeogene sands and clays during infiltration of recharge. Oxidation of sulphide minerals and release of minor quantities of Se in the Palaeogene deposits is a potential source, although desorption from Fe and Al oxides is also possible. A few samples from the Chalk outcrop area also had relatively high concentrations (1–2.6 μg L^{-1}), particularly groundwaters from boreholes that had been pumped for relatively short periods before sampling.

5.2.6 Iron and manganese

The presence of Fe and Mn in groundwater can be a useful indicator of redox status, although the dissolved concentration may be over-reported in water samples with a high particulate load due to the passage of fine colloidal particles through standard 0.45 μm filters. The concentrations of Fe were below detection limits in most samples, although the range of detection limits in the dataset was relatively large (5–30 μg L^{-1}). The generally low concentrations observed are as expected for oxic Chalk groundwater. One observation was 36,000 μg L^{-1} which strongly skews the population distribution (Figures 5.4 and 5.5). This was from a borehole at Ropley in the eastern part of the Chalk outcrop area. The redox status of this sample is somewhat uncertain since only a partial chemical analysis was attainable. The sample had a correspondingly high Mn concentration (726 μg L^{-1}). Although this would suggest a mildly reducing condition, the sample had a relatively high NO_3-N concentration (3.7 mg L^{-1}). By contrast, this suggests that conditions are oxic, as elsewhere in the Chalk outcrop area. The absence of Quaternary superficial deposits above the Chalk at this site would also appear to negate against a reducing condition. As the analysis is from archive data, the protocol for sampling is not clear. It is concluded that the observed high concentrations of Fe and Mn represent particulate and/or colloidal rather than truly dissolved fractions.

In all other samples, concentrations of Mn were low, although a substantial number had a comparatively high detection limit of 10 μg L^{-1}. All detectable Mn concentrations were 3 μg L^{-1} or less.

5.2.7 Other trace metals

Concentrations of Al are generally below the limit of detection with a few positive values in the east of the area, ranging up to 3.7 μg L^{-1}. Aluminium is typically present at low concentrations in Chalk groundwater because the alumino-silicate minerals are poorly soluble at circum-neutral pH. No Al data were available for the high-Fe, high-Mn sample from Ropley.

Almost all samples had Cd concentrations below detection limits (maximum detection limit 0.5 μg L^{-1}). The highest concentration was found in the sample from Ropley (2.44 μg L^{-1}). It is most likely that, as with Fe and Mn, this high concentration reflects particulate and/or colloidal components; the Cd is most likely to be adsorbed to oxide surfaces.

Concentrations of Co have a narrow range (5–95 percentile range 0.16–0.34 μg L^{-1}) with a near-linear probability distribution (Figure 5.5). Some of the higher concentrations occur in groundwaters from the eastern part of the part of the study area (Plate 4). Cobalt is probably derived primarily from iron oxides.

Concentrations of Cr are also generally low in the groundwaters. Observed concentrations vary over two orders of magnitude with a median value of 0.24 μg L^{-1}. Chromium is present in oxides and clays and desorption from these minerals under the ambient oxic conditions is a likely origin. Relatively low concentrations are found close the groundwater divide (Appendix 1, Plate 5) while higher concentrations are found in groundwater below the Palaeogene cover. The maximum observed concentration (2.9 μg L^{-1}) was from a borehole at Lower Upham on the southern edge of the study area.

Copper has a median concentration of 4.6 μg L^{-1} and a 5–95 percentile range of 1.3–18.2 μg L^{-1}. There is no apparent spatial trend in the concentrations (Appendix 1, Plate 5). Potential sources include iron oxides and clays though some contribution from copper pipes in the water distribution system may also be involved. However, the near log-linear data distribution on the probability plot for Cu (Figure 5.5) does not suggest that such a source has been significant. The highest concentration (32 μg L^{-1}) was from a borehole at Totford.

Lead concentrations have a 5–95 percentile range of 0.09–1.1 μg L^{-1} with a median of 0.3 μg L^{-1}. Generally the higher concentrations of Pb are observed across the northern part of the study area, the only samples with >1 μg L^{-1} occurring in boreholes at Overton and Axford.

Molybdenum concentrations are also low with a median of 0.043 μg L^{-1}. The highest concentration observed was from a borehole into the Chalk below Palaeogene cover at Timsbury, though the observed concentration is only 0.16 μg L^{-1} (Plate 6). Molybdenum mobility is likely to be controlled by sorption to oxides and clays, though some may be derived by oxidation of sulphide minerals.

Concentrations of Ni vary over an order of magnitude with a median concentration of 2.42 μg L^{-1}. Again, some of the highest concentrations are observed in groundwaters from below the Palaeogene cover in the south, although the observed maximum (10.9 μg L^{-1}) was from a borehole at West Ham Park in the northern outcrop area (Plate 6). Nickel is potentially derived from sulphide minerals including pyrite, as well as iron oxides. It may also derive from industrial or urban pollution. The relatively high concentrations from below the Palaeogene suggest a component derived from the overlying deposits. The relatively high concentration at West Ham Park may be influenced by pollution as it is within the Basingstoke urban area.

Concentrations of Sb are universally low with a 5–95 percentile range of 0.02–0.07 μg L^{-1} and a median value of 0.04 μg L^{-1}. Sources are likely to desorption from iron oxides or clays.

Uranium concentrations have a 5–95 percentile range of 0.16–0.38 μg L^{-1}. Possible sources include desorption from phosphate minerals and iron oxides. The highest concentration occurred at Timsbury in groundwater from below the Palaeogene cover, although this also had a relatively low concentration of 0.64 μg L^{-1}.

Vanadium concentrations likewise have a very narrow range with a low median concentration of 0.28 μg L^{-1}, as would be anticipated in Chalk groundwaters. Vanadium occurs as a minor constituent of iron oxides and in clays. No distinct spatial pattern is observed in V concentrations (Appendix 1, Plate 7).

Concentrations of Zn vary over two orders of magnitude with a median of 11.5 µg L^{-1}. The 5–95 percentile range is 3.2–39.2 µg L^{-1} although the observed maximum is 253 µg L^{-1}. Zinc occurs as a trace element in clays and in calcite and is typically present in higher concentrations than other trace cations at neutral pH. Zinc is also a common industrial metal and anthropogenic inputs may be significant close to urban areas or landfills. It may also be present in metal pipework and fittings on boreholes. Concentrations tend to be highest in the Chalk outcrop area around Basingstoke (Plate 7). The highest concentration occurs in a groundwater at Dummer, most likely due to contamination from pipework. The observed maximum is manifested as an obvious break in slope on the log-probability plot (Figure 5.5).

Concentrations of other analysed trace elements are low or below detection limits. These include the REE (rare-earth elements) which are typically low under near-neutral pH conditions, Tl which in all samples occurs at concentrations of 0.4 µg L^{-1} or less, Th of 0.08 µg L^{-1} or less, Nb concentrations <0.01 µg L^{-1} and Cs concentrations of <0.02 µg L^{-1}.

5.3 GROUNDWATER EVOLUTION ALONG FLOWLINES

The evolution of groundwater chemistry in the main part of the aquifer can be illustrated by evaluating the changes in quality from the groundwater divide southwards to the edge of the outcrop. Two groundwater flowlines were assessed (Figure 5.6). The first was from Ibthorpe and Vernham Deane to Timsbury along the line of the Test valley (Figure 5.7) and the second was from Dummer to Otterbourne in the River Itchen catchment (Figure 5.8).

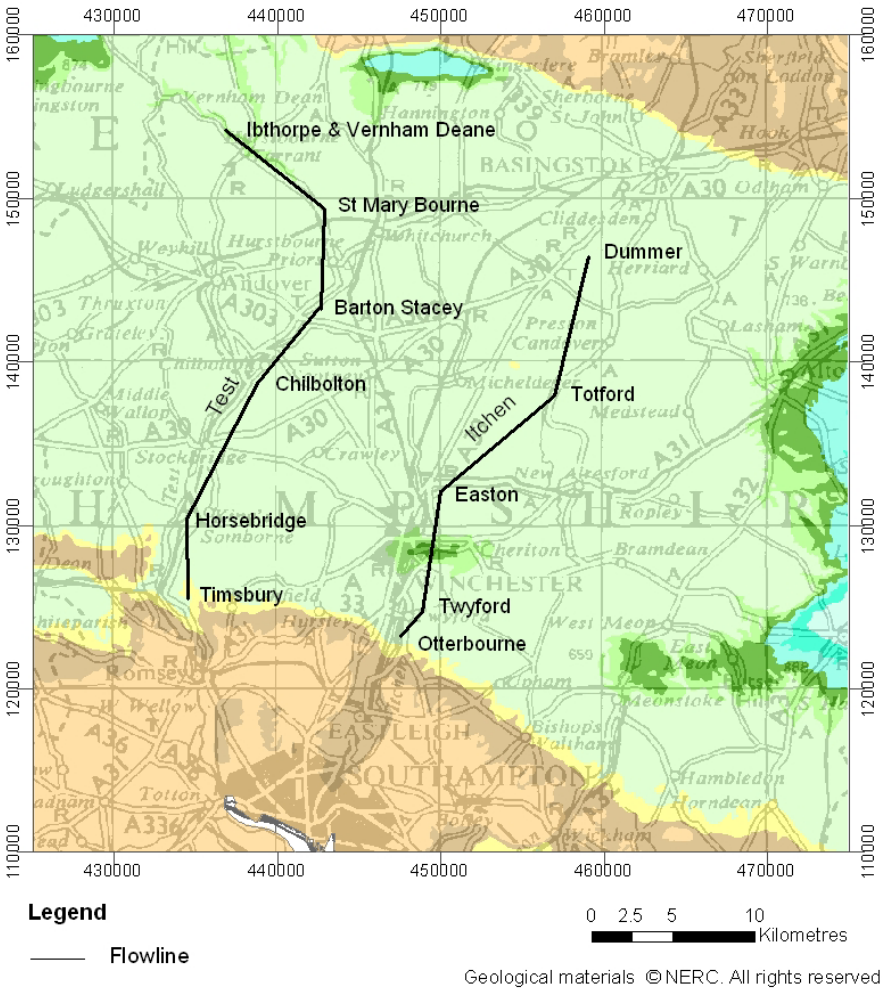

Figure 5.6 Groundwater flowlines along the River Test and Itchen valleys

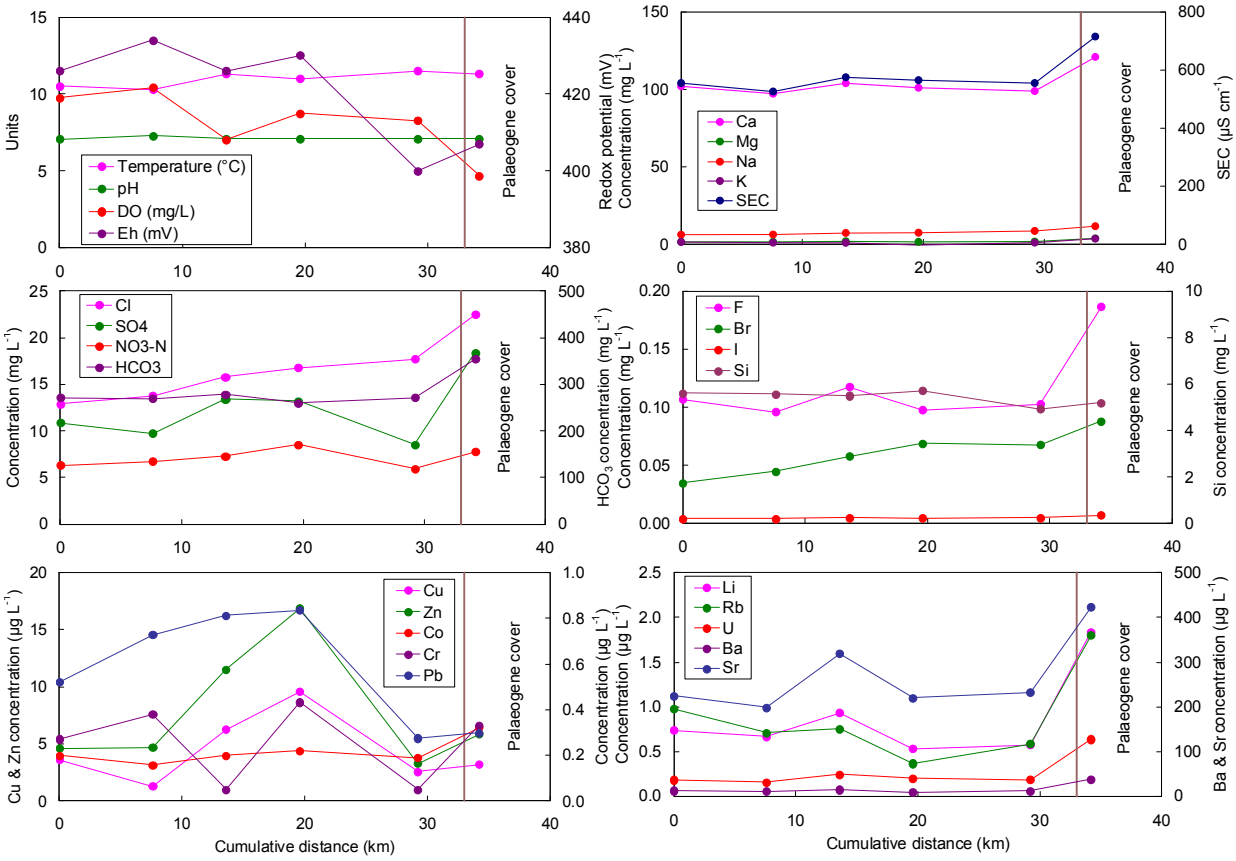

Figure 5.7 Chemical characteristics of Chalk groundwaters along a line of flow from Ibthorpe & Vernham Deane to Timsbury (River Test catchment). Palaeogene cover extends 1 km north of Timsbury

The two flowlines show similar chemical features which include:

- little lateral variation in chemistry within the Chalk outcrop area;
- maintenance of oxic conditions below the Palaeogene cover albeit with slightly lower concentrations of dissolved oxygen and lower redox potential;
- increase in concentrations of major ions (becoming more marked below the Palaeogene cover in the Test valley);
- little lateral variation in concentrations of nitrate;
- increase in concentrations of F, Br, Li, Rb, U, Ba, and Sr in groundwaters below the Palaeogene cover;
- variable concentrations of trace metals, particularly Pb and Zn, with a reduction in concentration below the Palaeogene edge.

5.4 ISOTOPIC COMPOSITION

Observed compositions of $\delta^{18}O$ lie in the range -7.3 to -6.2 ‰ and of $\delta^{2}H$, -46.1 to -40.4 ‰. These values are consistent with compositions of recently recharged groundwaters analysed in the Hampshire area (Darling et al., 2003; Darling et al., 2005). A plot of $\delta^{18}O$ against $\delta^{2}H$ (Figure 5.9) shows that all but two groundwaters lie close to the Meteoric Water Line and the values are generally in agreement with those for the average yearly rainfall in the area (Darling and Talbot, 2003).

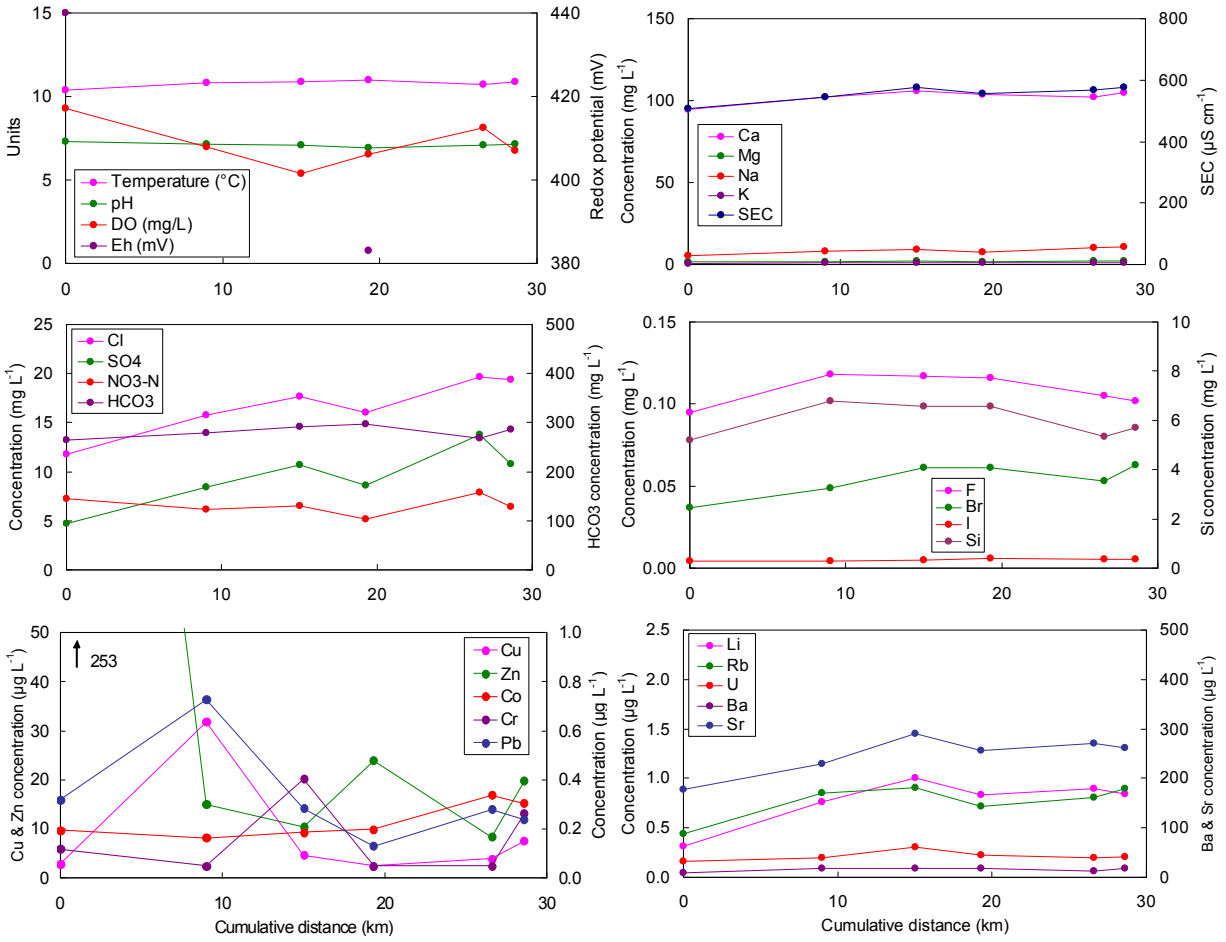

Figure 5.8 Chemical characteristics of Chalk groundwaters along a line of flow from Dummer to Otterbourne (River Itchen catchment. All sites on outcrop chalk.

For the Chalk, $\delta^{13}C$ can be a sensitive way of assessing the extent of the interaction between the water and the matrix (Darling et al., 2005). In the Hampshire Chalk, $\delta^{13}C$ compositions range between -17.4 ‰ and -9.36 ‰. The most depleted signatures are from sites in the north of the area, close to the groundwater divide and suggest these groundwaters have had a relatively short residence time in contact with the aquifer matrix. Percolating groundwater acquires dissolved inorganic carbon through reaction of the rock carbonate with dissolved soil-derived carbon dioxide. The isotopic composition of the resulting dissolved inorganic carbon is between that of the soil CO_2 (close to -26 ‰) and marine carbonate (close to 0 ‰). Re-equilibration with excess soil-derived CO_2 leads to rather more negative values in the unconfined aquifer. The slightly enriched compositions of groundwater from Newtown [SU 612 126] suggest longer residence time for groundwaters below the Palaeogene cover.

Under confined conditions excess CO_2 is consumed and solution-reprecipitation reactions drive the $\delta^{13}C$ towards the rock value. However it seems unlikely that the relatively enriched composition at Andover (-9.36 ‰) in the unconfined aquifer is due to this process as a value of above -10‰ in the unconfined aquifer would be anticipated to represent a bulk age of a few thousand years. The Andover borehole was not exceptionally deep and the reason for this anomalous value is unclear.

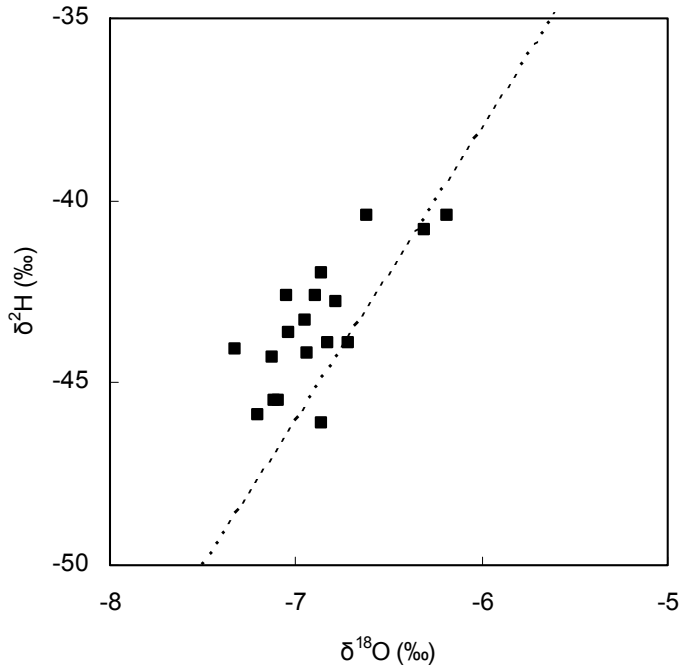

Figure 5.9 O and H stable-isotopic composition of the groundwaters of the Hampshire Chalk (dotted line shows the global meteoric water line of Craig, 1961)

5.5 CHEMICAL VARIATIONS WITH DEPTH

Variation in water chemistry with depth in the Chalk can be assessed from data provided from previous studies of three sites (Figure 5.10). The earliest work to assess groundwater depth profiles was carried out in the unsaturated zone at Bridget's Farm near Winchester by the Water Research Council (WRc) in the 1970s as part of their research on nitrate in groundwater (Young and Gray, 1978; Young et al., 1976). In addition to NO_3, NO_2, Cl, Ca, and tritium were determined. This research found high concentrations of NO_3-N in porewaters from the unsaturated zone, reported to be equivalent to 50% of total fertilizer applications in the preceding three decades. The work related high concentrations to arable land use and ploughing of grass leys, and also enabled some of the first predictions of future trends in nitrate concentrations in groundwater. The work at this site was followed by profiling of the unsaturated and saturated zones by BGS in 1994 (Coleby et al., 1998), for NO_3, SO_4 and Cl as part of a study on the evidence for denitrification in the unsaturated zone.

Kinniburgh and Trafford (1995) studied the impact of afforestation on porewater chemistry in the Chalk unsaturated zone beneath a mature beech wood at Black Wood, near Micheldever. The rate of nitrate leaching was estimated to be about 20-30 kg ha^{-1} yr^{-1}, but was double this in cleared areas. The majority of the porewater profiles were for the uppermost 10 m, but there was some evidence that nitrate concentrations were low below 30 m depth. Concentrations of nitrate in porewater close to the exposed western edge of the woodland were also very low. However, concentrations of a number of solutes were higher, including Na, Cl, Mg and SO_4. This was taken to be from a combination of evaporation and dry deposition.

The relationship between chalk lithology and porewater chemistry was investigated by Stuart et al. (2008a) in a detailed profile of an 80-m deep borehole at Twyford (Figure 5.11). The results indicated that there do not appear to be any zones of unfractured chalk where porewater has retained pre-1960s concentrations of nitrate.

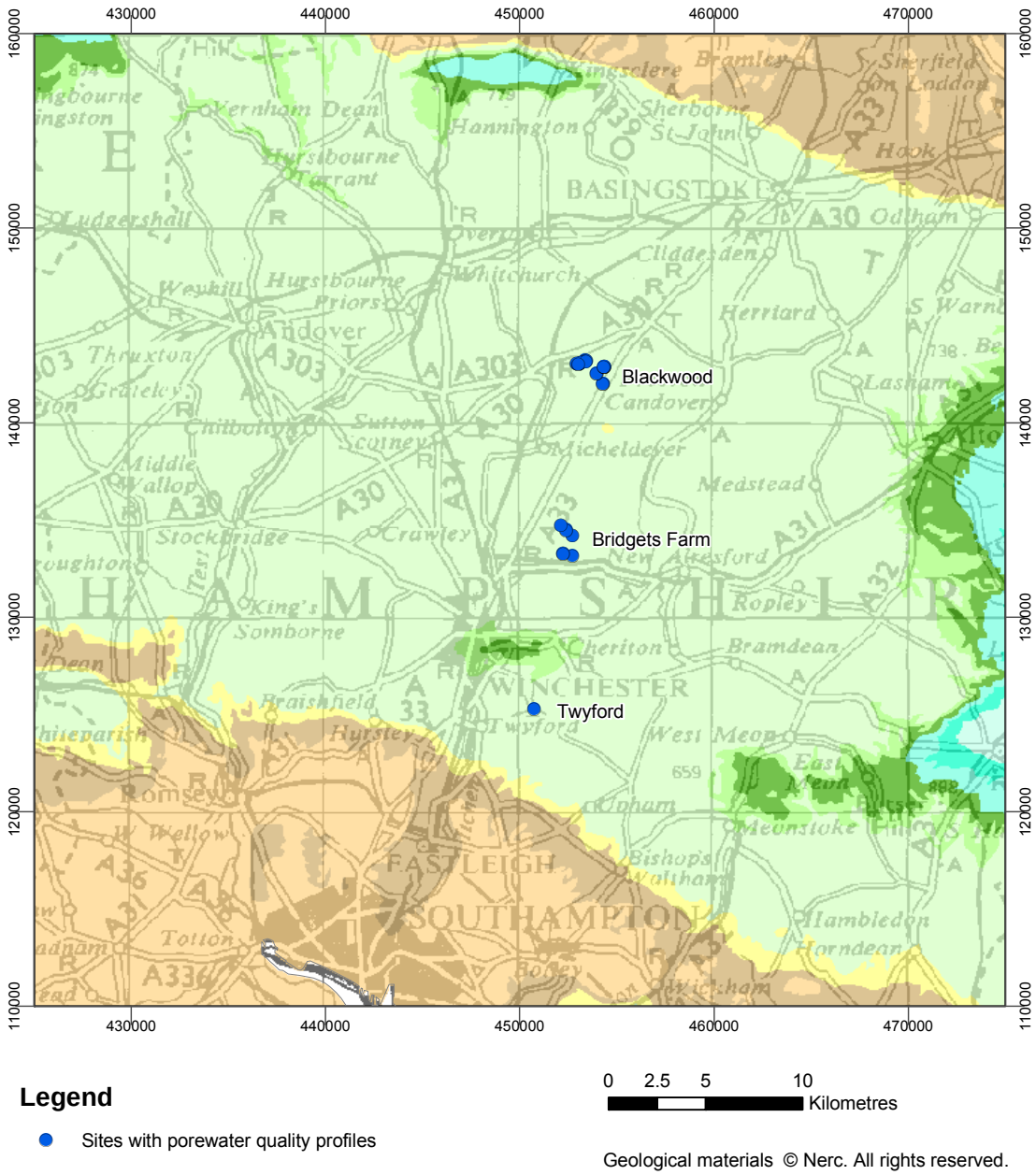

Figure 5.10 Locations of sites with depth profiles of porewater quality

Porewater NO_3-N concentrations followed a typical profile for chalk overlain by arable land except in a 15 m-thick zone of the Lewes Nodular Chalk Formation, where a number of marl bands appear to result in a zone of slow-moving water with low nitrate concentration but elevated concentrations of some trace elements (including Co, Mo, Sb and U) possibly associated with clay minerals.

Figure 5.11 shows the vertical profiles for NO_3-N, Cl, HCO_3 and K as well as the trace elements Sb, F and Fe. The nitrate-N profile shows that concentrations are relatively high in the unsaturated zone, in many cases exceeding the drinking water limit of 11.3 mg L^{-1} as N. A sharp transition in NO_3-N concentration occurs at or about the water table, with a steady decline below. In the zone 52–62 m below surface, NO_3-N concentrations are very low but increase slightly in the zone 65–75 m depth.

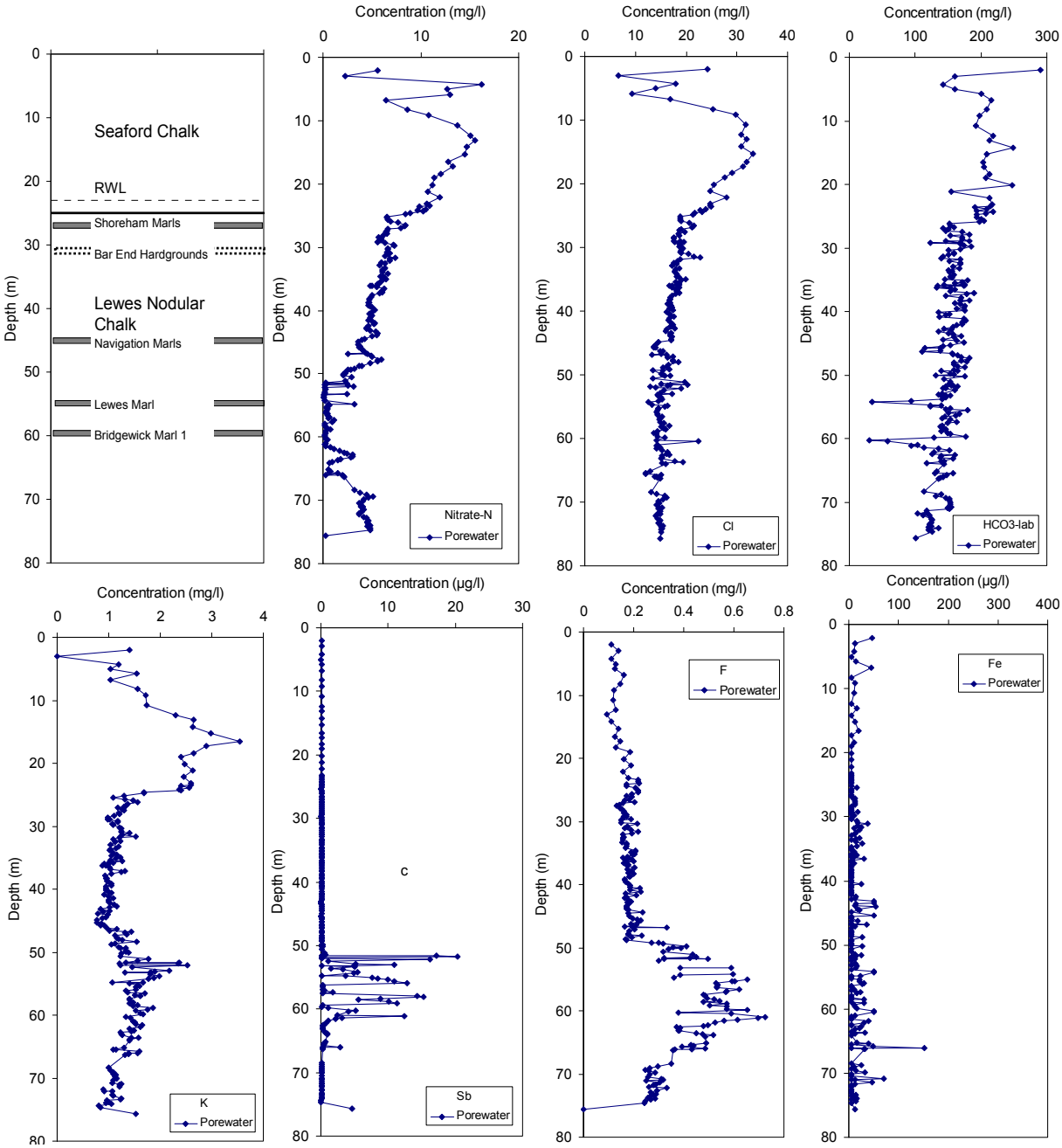

Figure 5.11 Porewater quality profiles from the Twyford borehole

Chloride and Na (the latter not shown) have profiles of similar shapes with higher concentrations in the unsaturated zone and less-variable concentrations below this. Calcium and HCO_3 also have similar profiles but both show two sharp falls in concentration at about 54 m and 60 m. The origin of these less-mineralised waters is unclear. A group of parameters (K, Rb and SO_4) also have similar profiles but exhibit a number of sharp peaks in the zone 52 m to 65 m.

The trace elements U, Sb, Mo, Co and Br are present at low or very low concentrations throughout the porewater profile, except in this same 52–65 m zone. High concentrations in this zone are also observed for the elements F, Si, Li and Sr. Interaction with clays and metal oxides is a likely cause of the increased concentrations. There is no evidence of reducing conditions from iron and manganese concentrations.

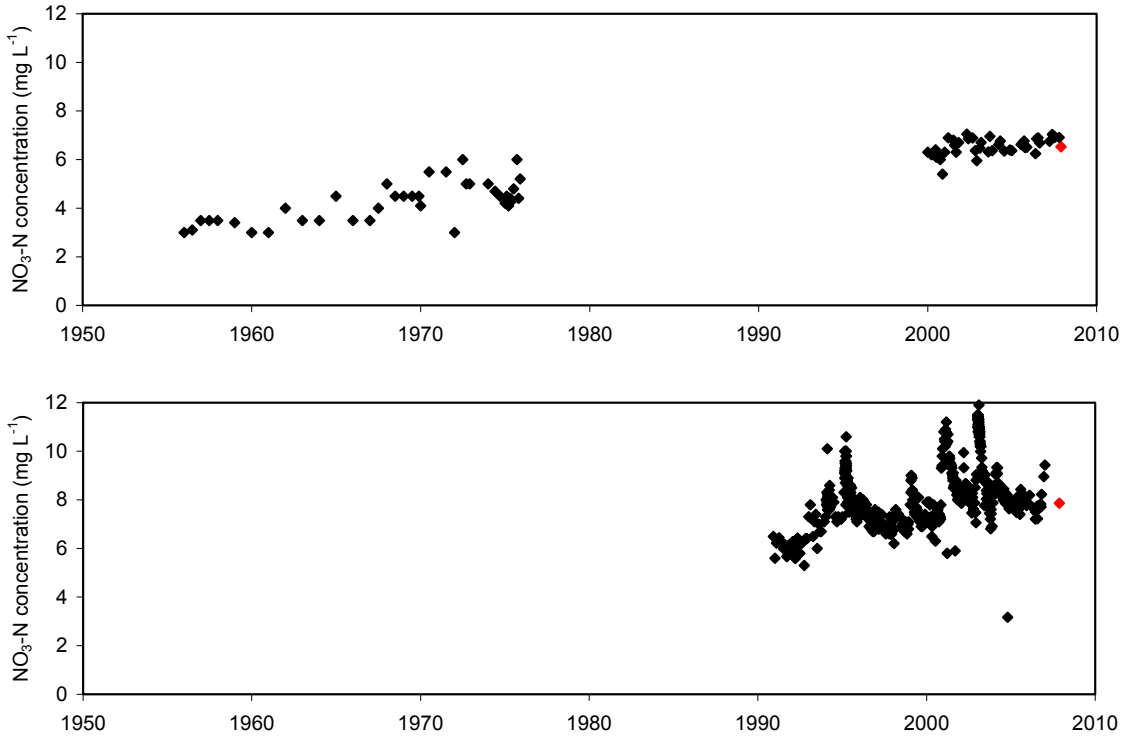

Figure 5.12 NO_3-N time-series data for two public-supply boreholes in the Hampshire Chalk. Data for the upper series are from Young et al. (1976) and the site owner (unpublished); data for the lower series from Stuart et al. (2008b). Data in red are from the present study

5.6 TEMPORAL VARIATIONS

In the few boreholes for which records exist, NO_3 concentrations have shown a slow but steady increase since the 1950s (Figure 5.12). This is generally considered to be due to the post-war intensification of agriculture and applications of nitrogenous fertiliser to farmland. At some sites in the study area, concentrations now exceed the drinking-water limit of 11.3 mg L^{-1} as N). Concentrations at some sites vary seasonally (Figure 5.12), being higher in the winter and spring when the water levels are typically higher. Such peaks can provide significant problems for water utilities.

6 Baseline groundwater chemistry

6.1 EXTENT OF ANTHROPOGENIC INFLUENCES

Human impacts are mainly visible in the presence of indicator contaminants such as nitrate from agriculture and some trace metals from urban or industrial uses.

Nitrate is highly mobile and its widespread presence at concentrations well above the estimated baseline range, together with the observed increases in concentration over the past two decades, indicates the extent to which the aquifer is now influenced by farming practices. Baseline concentrations are likely to be of the order of 3–4 mg L^{-1} as N. At one site the concentration exceeded the drinking-water limit at the time of sampling though the time-series data indicate that other sources may in time exceed the limit without remediation steps. The whole outcrop of the Hampshire Chalk was designated as a Nitrate Vulnerable Zone in 2009 under the latest review of the implementation of the Nitrates Directive (Defra, 2009). This includes the application of the Code of Good Agricultural Practice to be followed by all farmers and a mandatory Action Programme of measures for the purposes of tackling nitrate loss from agriculture.

Other nitrogen species, NO_2 and NH_4, are present at above baseline concentrations in groundwater in the south-east of the study area, particularly the Meon valley. Phosphorus concentrations are also elevated in the same area.

Some boreholes have groundwaters with relatively high concentrations of Cu and Zn, although this may be due to contamination from wellhead pipework rather than reflecting concentrations in the aquifer. Anomalous concentrations of Fe, Mn and Cd in some samples are likely due to a non-solute contribution (i.e. particulate/colloidal matter in one sample). However, no evidence was found of widespread contamination from point sources or urban environments.

6.2 REGIONAL BASELINE CHARACTERISTICS

The ‘baseline composition’ of the groundwaters in the study area spans a limited range for many elements, but may span an order of magnitude for some determinands, as a result of natural geochemical processes. For most determinands, the upper limit on ‘baseline’ concentrations has been estimated as the 95th percentile value. For most determinands, this removes the obvious outliers where they exist. As noted above, NO_3-N, which is mainly derived from agricultural activity, is an exception to this with 84% of samples exceeding the estimated baseline range of 3–4 mg L^{-1}.

Rainfall chemistry influences are apparent in generating the chemical background of constituents such as Cl. No decline in concentrations away from the coast is seen. Groundwater concentrations are higher than the evaporated rainfall concentrations shown in Table 3.1, suggesting an evaporation factor of around 5 or 6 (discounting effects of dry deposition).

The Ca-HCO_3 compositions are typical of unconfined Chalk groundwater. Chalk equilibrium reactions produce a hard water where Ca predominates over other cations and HCO_3 is the main anion. Variations in the natural chemistry take place with increasing residence time as water moves away from the groundwater divide and as water moves beneath the Palaeogene cover.

There is a notable effect in chemistry from the Palaeogene cover in the south of the study area. This is typically thin and variably permeable so will allow some recharge through

vertical leakage. The presence of the overlying Palaeogene deposits appears to be responsible for increased concentrations of Mg, K, SO_4, Br, F, Ba, Sr, Li, Rb, Se, Cr, Mo, Ni, U. While these all depart from the typical baseline concentrations of the Chalk groundwater, they also represent baseline conditions according to our definition as they are not of anthropogenic origin.

The median concentrations for most determinands are similar to those measured for the adjoining Dorset Chalk. The data are reported slightly differently for this area with the 97.7th percentile rather than the 95th used in this study. However, it is clear that there are fewer high values for many determinands in the Hampshire Chalk than in Dorset. This probably reflects both the increased distance from the coast and the smaller proportion of sites abstracting from beneath the Palaeogene cover.

Individual values for a few determinands exceed the maximum values allowed for drinking water. These include NO_3-N, Fe and Mn. The latter two elements are taken to be predominantly of natural origin.

7 Conclusions

The Chalk aquifer of Hampshire contains groundwater of predominantly good inorganic quality. The chemical compositions have been assessed and baseline compositions defined by a combination of statistical distributions, spatial variation, location with respect to overlying rock strata and time-series variability. For many elements, the 95th percentile (P_{95}) has been taken as a first approximation to the upper end of a baseline concentration range as this eliminates obvious outliers with anomalously high concentrations. Tables of statistical data distributions, box plots and cumulative-probability diagrams show the variability in compositions within the aquifer.

The inorganic chemistry of the groundwater is controlled largely by rainwater reacting with the Chalk. Calcite dissolution dominates the groundwater chemistry, resulting in Ca-HCO_3 waters. These have relatively uniform major-element chemistry. Variations in the natural chemistry take place with increasing residence time as water moves away from the groundwater divide and as water moves beneath the Palaeogene cover. The presence of the overlying Palaeogene deposits has resulted in increased concentrations of a wide range of determinands.

Anthropogenic inputs have also influenced the groundwater compositions in the study area and the effects of agricultural inputs are most obvious from the presence of NO_3 in the groundwater. Concentrations exceed the drinking-water limit of 11.3 mg L^{-1} (as N) at one site, probably reflecting the intensification of agriculture in the study area during the last few decades. Phosphorus concentrations are also relatively high in some samples.

No evidence was found of widespread contamination from point sources or urban environments. Concentrations of trace metals (Zn and Cu) are present at elevated concentrations in some boreholes, although this may be due to contamination from wellhead pipework rather than reflecting concentrations in the aquifer.

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Appendix 1 Spatial distribution of solute concentrations in groundwater of the Hampshire Chalk

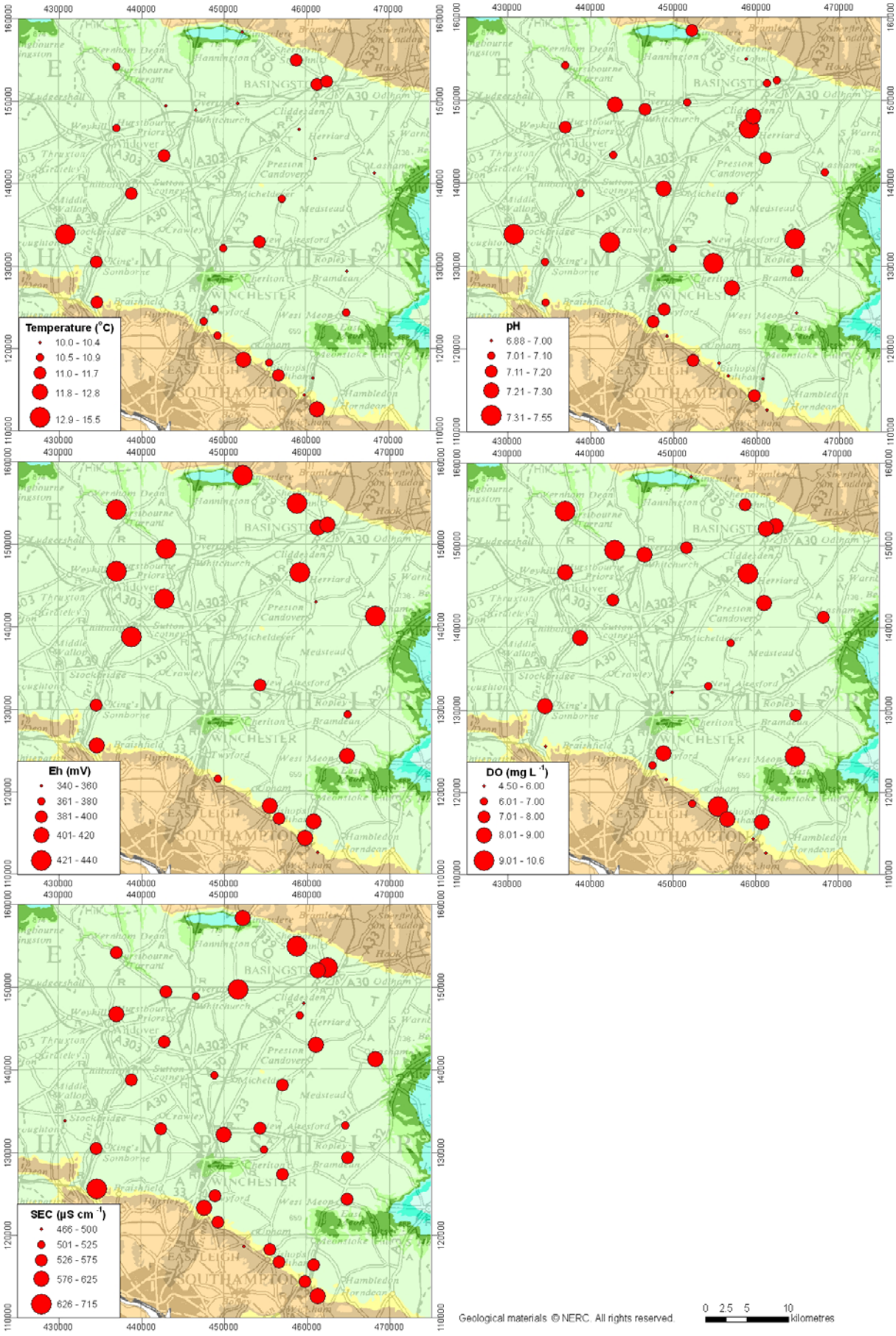

Plate 1 Distribution of field-determined parameters

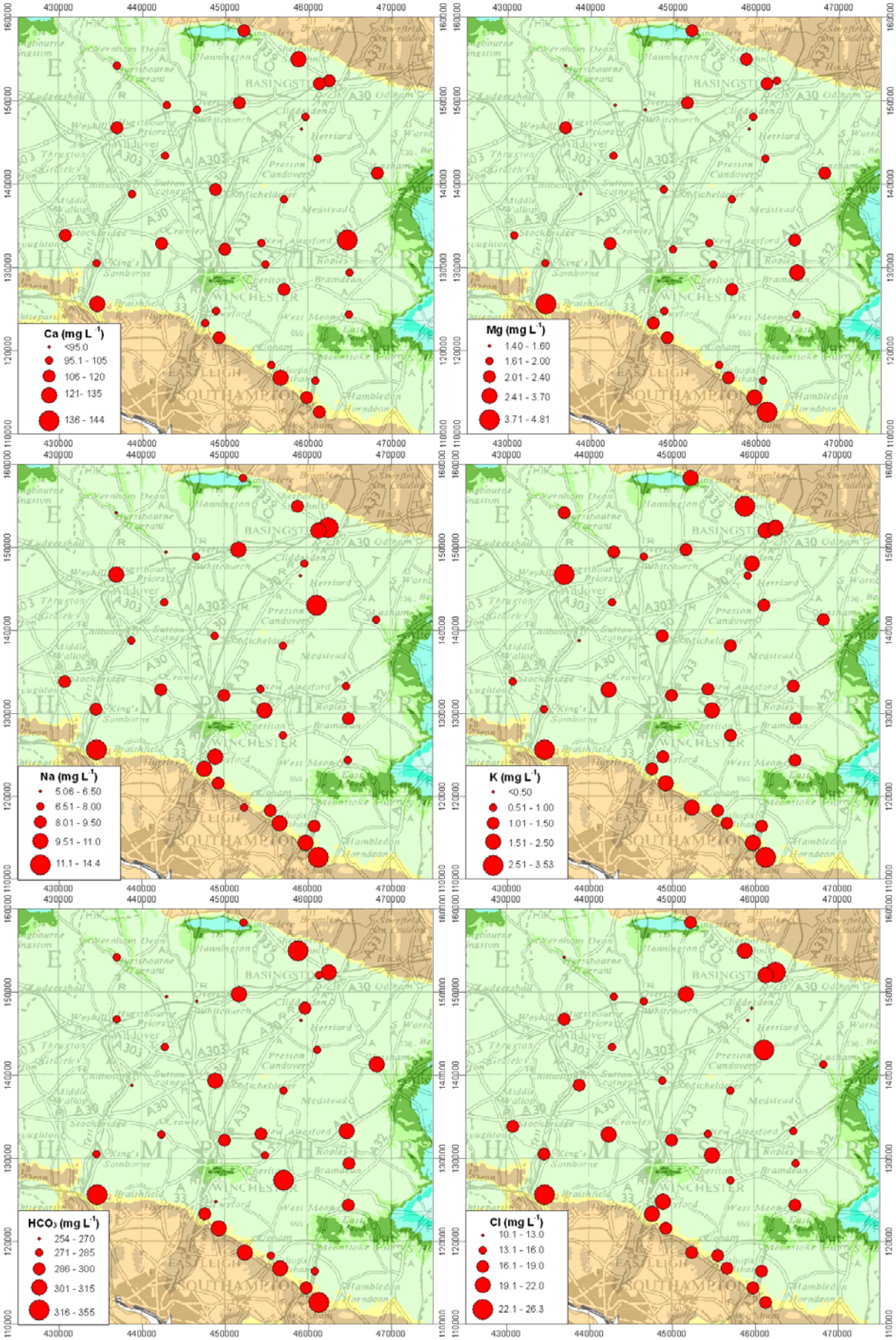

Plate 2 Distribution of major ions and nitrogen species (continued)

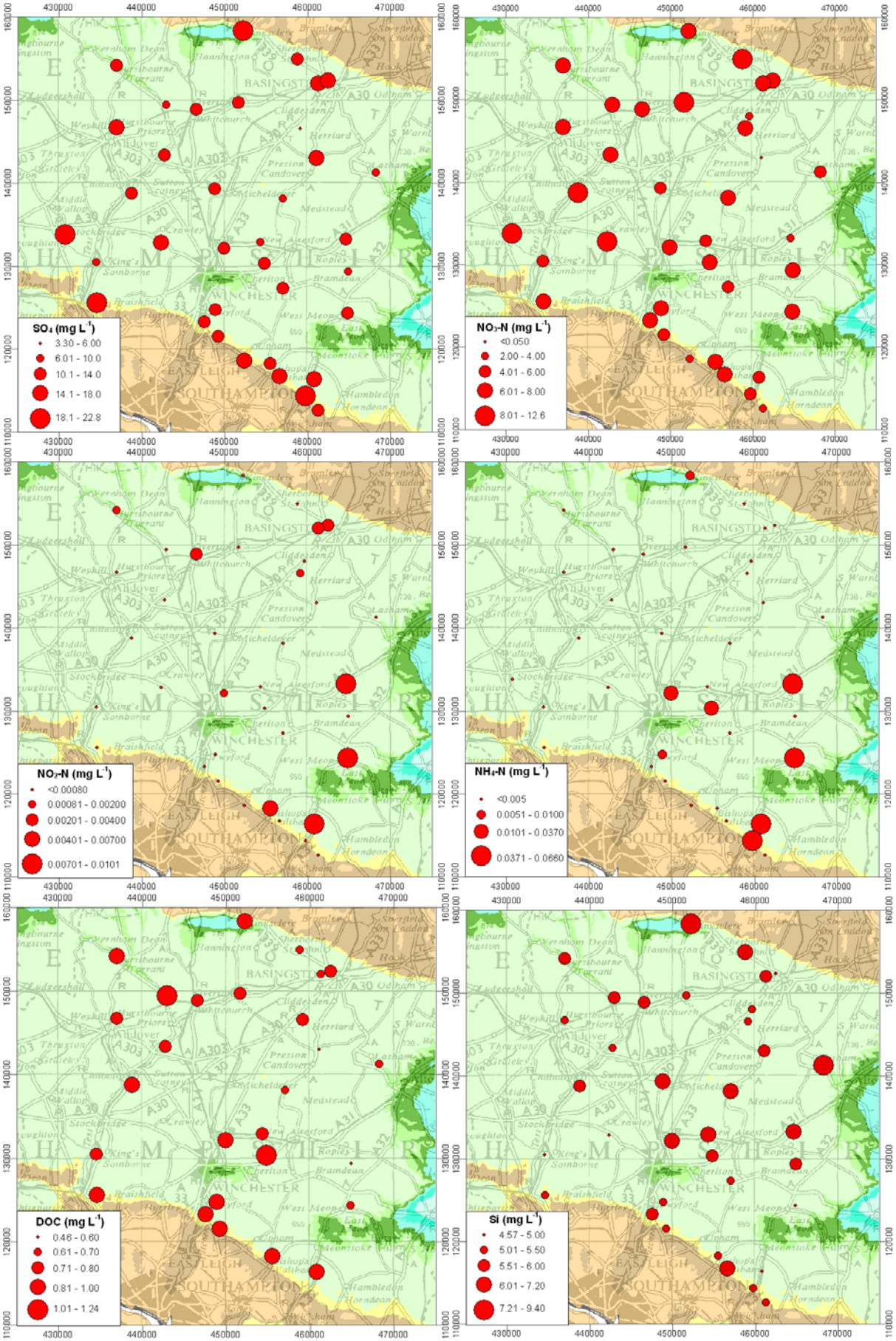

Plate 3 Distribution of major ions and nitrogen species (continued)

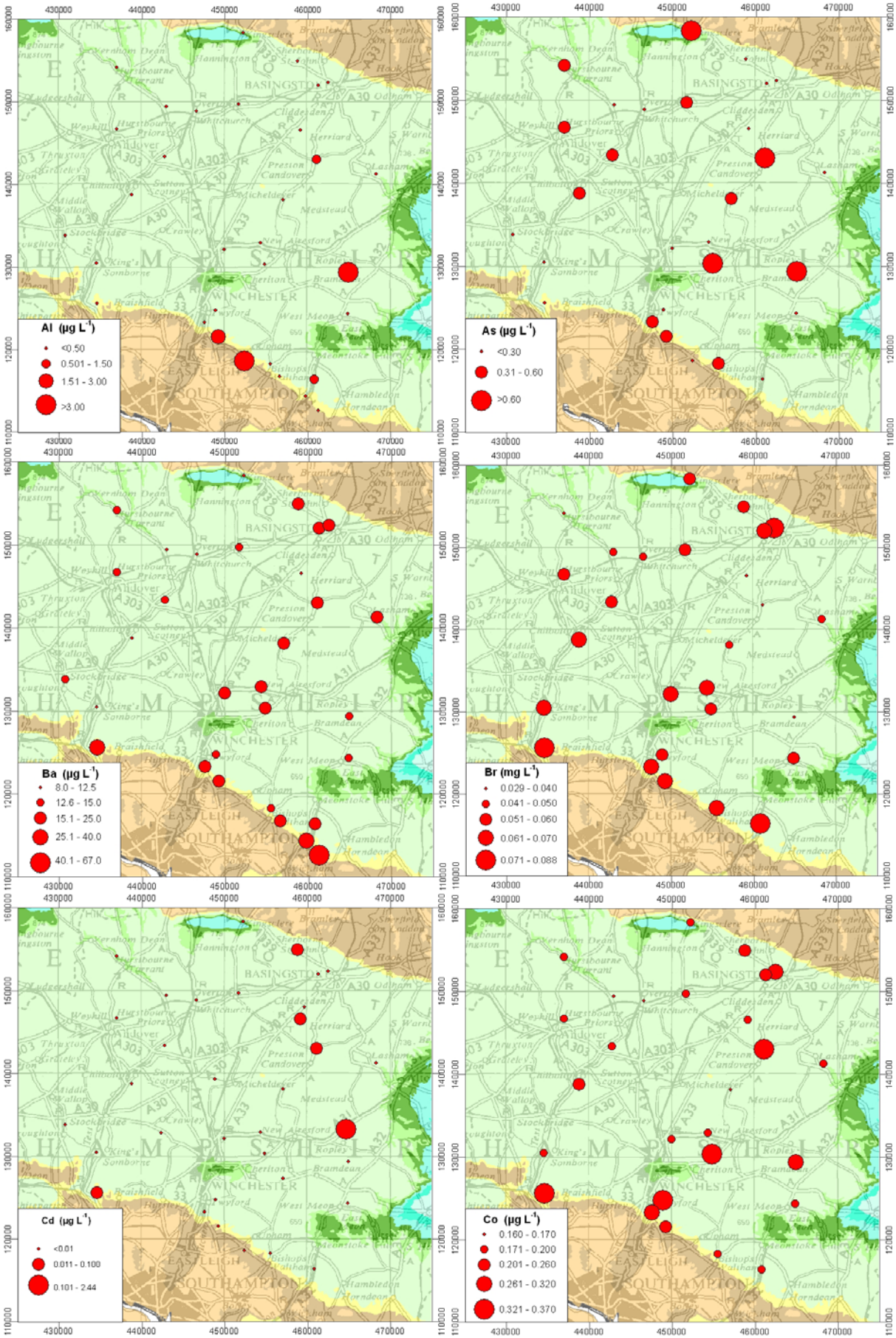

Plate 4 Distribution of trace elements (continued)

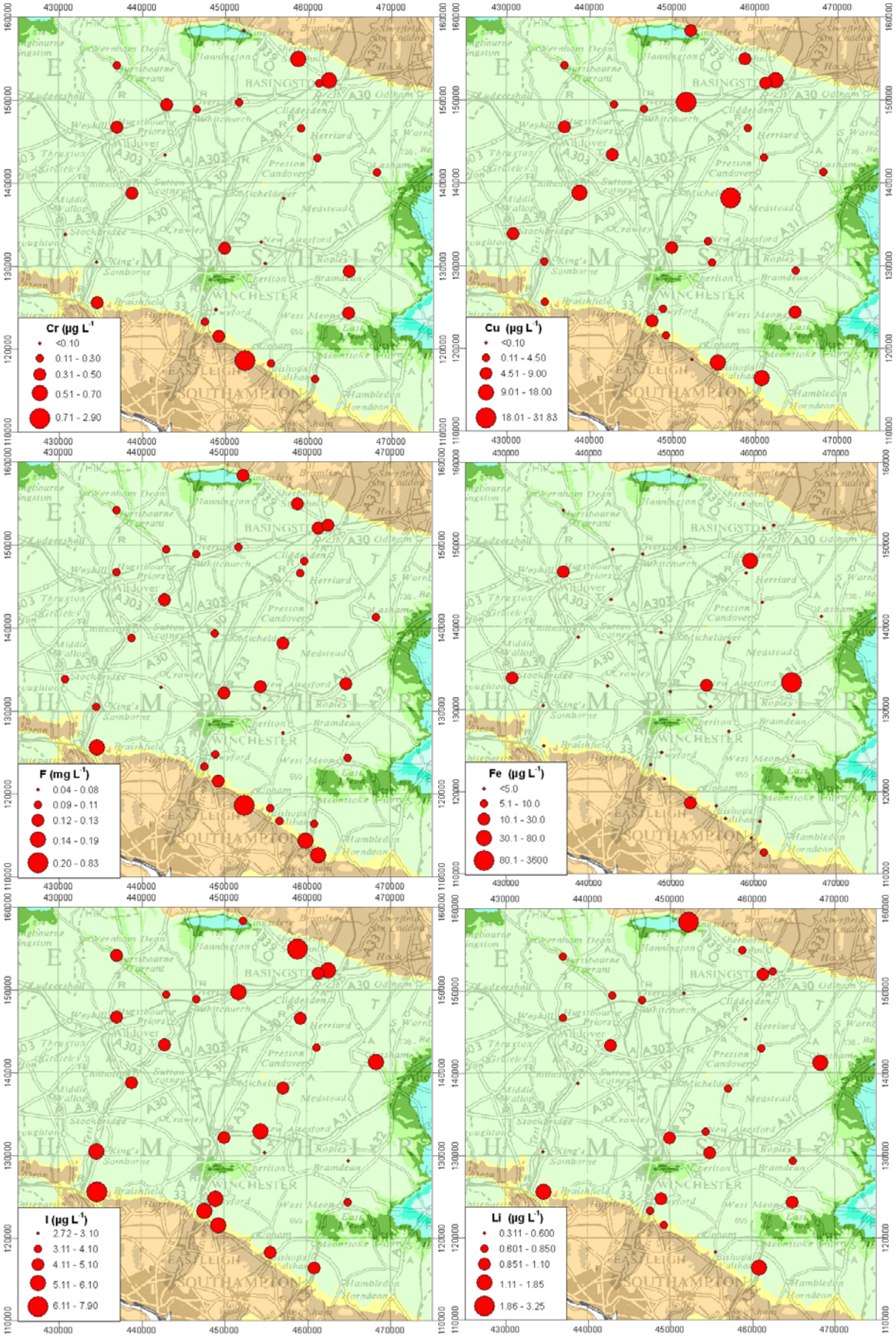

Plate 5 Distribution of trace elements (continued)

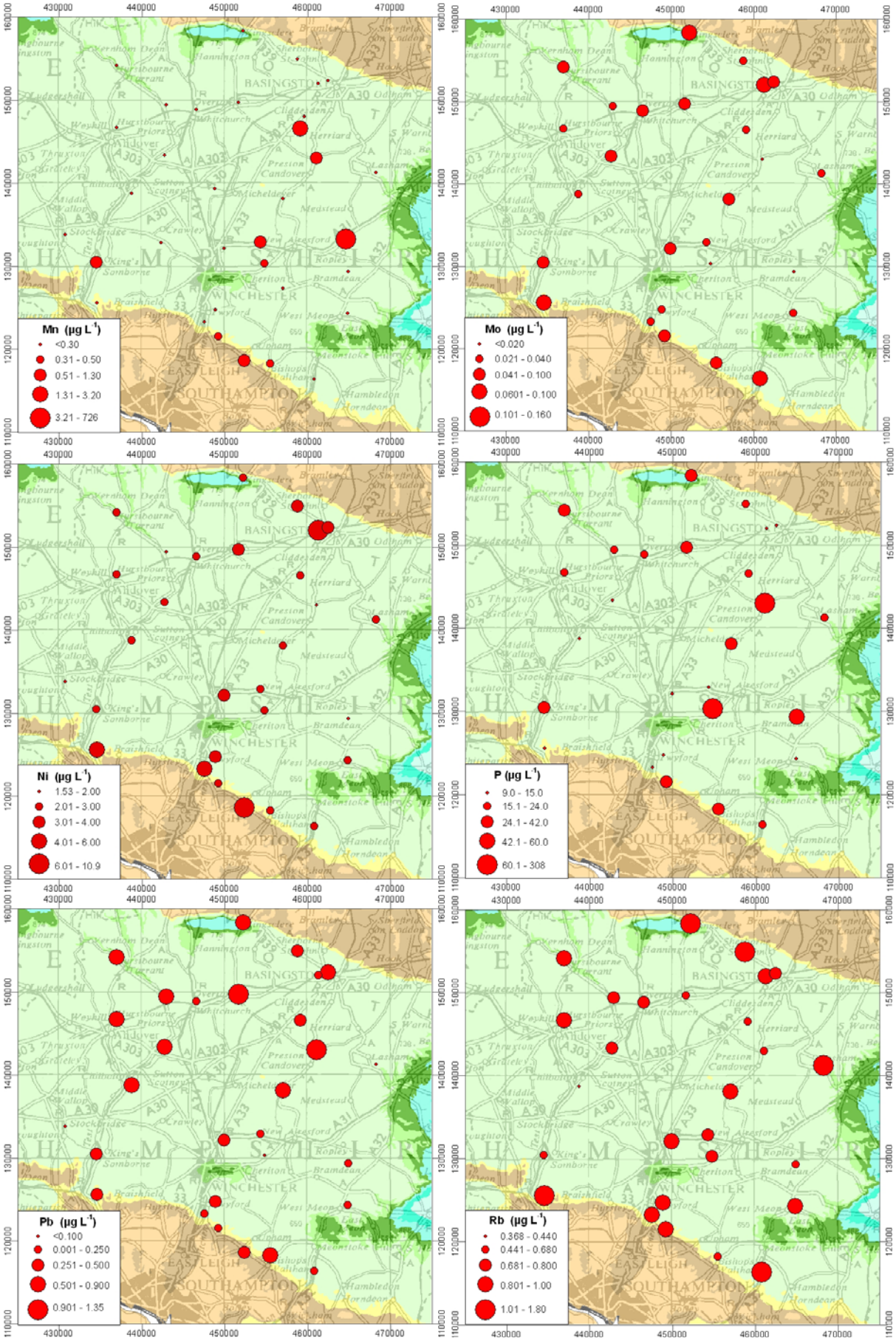

Plate 6 Distribution of trace elements (continued)

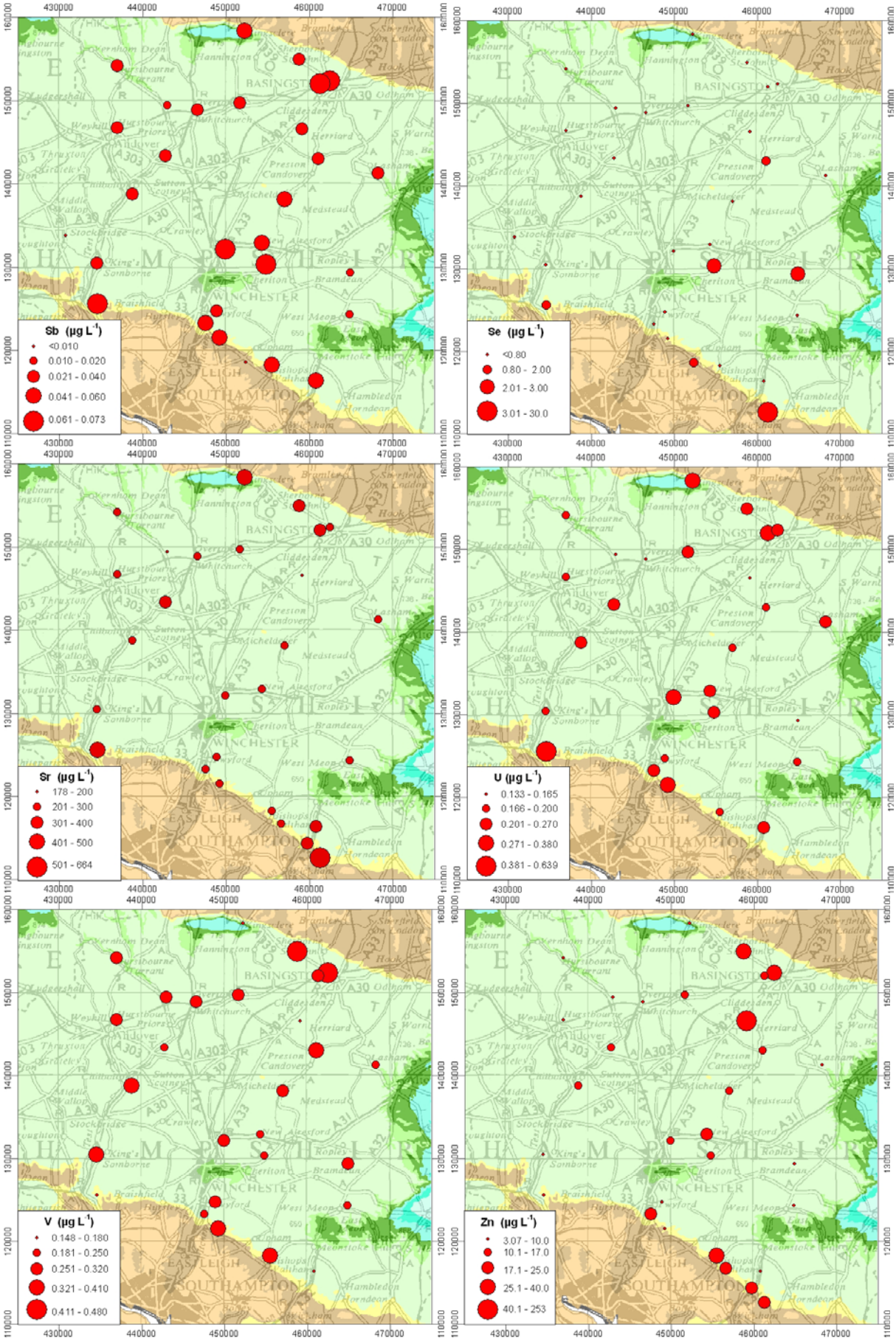

Plate 7 Distribution of trace elements (continued)